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ERRATA.

Page 48, last line,	for vl/ν read vd/ν .
Page 49, line 1,	for $\log(vl/v)$ read $\log(vd/v)$.
Page 49, line 17,	for 0.25 read 0.208.
Page 49, line 20,	for 0.0191 read 0.0159.
Page 49, line 3 from bottom,	for 0.0382 read 0.0318.
Page 491	
Page 50 lower part, in equation	s, for l read, 2l.
Page 52 J	
Page 518, line 10,	for the International system, etc., read Row-
	land's system, of 3303:10 and 3302:49.
Page 518, line 20,	for 3302:96 read 3303:10.
Page 519, line 9,	for sodium read zinc.
- mg / 020, 12110 0,	I for zinc read sodium.
And on Plate 8,	for 3302:70 read 3302:49.

PROCEEDINGS OF

THE ROYAL SOCIETY.

SECTION A.—MATHEMATICAL AND PHYSICAL SCIENCES.

On the Interpretation of the Indications of Atomic Structure Presented by Crystals when Interposed in the Path of X-Rays.

By WILLIAM BARLOW, F.R.S.

(Received June 22,-Read June 25,-Revised August 20, 1914.)

W. L. Bragg states in his exposition of the method of investigating the structure of crystals by means of X-rays, that a slight symmetrical distortion of the arrangement of the atoms, which would reduce the crystal symmetry, would not affect any of the results that he had just been describing. Advancing considerably beyond this conclusion, it is proposed to show that a large amount of a certain kind of deformation of an atomic system arranged according to either of the three space-lattices possessing cubic symmetry, considerable enough to profoundly alter the nature of the arrangement, can take place without any appreciable evidence of this deformation being presented by the X-ray results. The argument consists of the proofs of the following propositions:—

Proposition 1.—Each of the three space-lattices which possess cubic symmetry can, by a simple modification, be converted into a regular point-system having this symmetry, but the system of trigonal axes of which, unlike that of the space-lattice, is of the non-intersecting kind.† The method employed to effect this modification is to so select one-fourth of the trigonal axes of the space-lattice concerned that no two of the selected axes

^{* &#}x27;Roy. Soc. Proc.,' A, vol. 89, p. 275.

[†] The system of non-intersecting axes of cubic symmetry is described by Barlow in Groth's 'Zeitschrift für Krystallographie,' vol. 23, p. 7 (figs. 1-3), also by Barlow and Pope, 'Trans. Chem. Soc.,' vol. 91, p. 1183.

intersect, and then to destroy the remaining three-fourths by symmetrically shifting each point of the space-lattice to the same extent in the appropriate direction along the selected trigonal axis on which it lies, and consequently away from the three other trigonal axes which passed through it. In the cases of the cubic space-lattice and the cube-centred space-lattice, the shifts can take place in both directions on an axis or in one only. The effect of any such symmetrical displacement of the points is that each of the selected axes continues to be a trigonal axis of the system of points, while each of the remaining three-fourths of the trigonal axes ceases to be so. The system of points resulting has cubic symmetry, but in nearly all the cases this is of a lower class than that of the space-lattice from which it is derived.

[Added July 20.—The following proof of this proposition is offered:—

Two of the three kinds of space-lattice referred to can each be regarded as consisting of interpenetrated component space-lattices of the remaining kind. Thus—(a) The points of the cubic space-lattice can be divided symmetrically into two identical sets in such a way that four of the eight points found at the corners of each cubic element are allotted to one set and the remaining four points to the other, each set of four thus allotted lying at the corners of a regular tetrahedron. The arrangement presented by half the points of the cubic space-lattice thus selected is easily seen to be that of the points of the face-centred lattice in which each point is equidistant from 12 nearest surrounding points. (b) The cube-centred space-lattice consists of two interpenetrating identical cubic space-lattices so related that the points of one of them lie at the centres of the cubic cells marked out by the points of the other. And since each cubic space-lattice is composed, as just pointed out, of two identical interpenetrated face-centred lattices, it follows that the cubecentred space-lattice consists of four symmetrically interpenetrated identical face-centred space-lattices. For the purposes of Proposition 1 the cubic space-lattice and the cube-centred space-lattice can therefore both be regarded as consisting of component face-centred space-lattices, and the proof of Proposition 1 for the latter which follows is easily extended to establish its validity for the other two space-lattices of the cubic system.

As to the application of Proposition 1 to the face-centred space-lattice:—
The system of non-intersecting trigonal axes of the cubic system can be generated from two non-intersecting axes the directions of which are inclined to one another at the angle subtended by two body diagonals of a cube. The process consists in continually locating additional axes of the same kind in such positions with respect to the two given axes and also to those from time to time added, that ultimately trigonal rotations through 120° made about any

one of the axes present become coincidence-movements of the unlimited system produced. The method is traced in detail in the journals just referred to.* The process indicated is available for the selection of one-fourth of the trigonal axes of the face-centred lattice required in Proposition 1 and when this selection has been made the coincidence-rotations proper to the system of non-intersecting trigonal axes thus located can be applied to the position after shift of a single point of the space-lattice in order to locate corresponding similar shifts of the remaining points consistent with the coincidencemovements in question. This is possible because the shifts take place along. the selected trigonal axes; a condition which prevents the points of the point system generated by the coincidence-rotations from being more numerous than those of the space-lattice concerned. The direction of shift of one point of the face-centred lattice along its trigonal axis determines the direction of shift of every other point on its trigonal axis. The point-system generated from the single shifted point by carrying out the coincidence-rotations thus gives the result of making all the shifts prescribed in Proposition 1 symmetrically in harmony with the system of non-intersecting trigonal axes and presents the cubic symmetry proper to the system of rotations about these axes; the homogeneous structure obtained is that designated Type 1 in Barlow's list+ and displays tetartohedral crystalline symmetry. The unaltered face-centred space-lattice is of type 8a1, which possesses holohedral crystalline symmetry.

As to the remaining two space-lattices of cubic symmetry:-

The method described of obtaining a regular point-system of cubic symmetry from a space-lattice can be applied to a cubic space-lattice in two different ways. For if, as above explained, we regard this lattice as composed of two interpenetrated face-centred lattices, the points of one component system found on a given trigonal axis may (1) move in the same direction as those of the other present on this axis, in which case, if the movements are equal, they will preserve an equal spacing on this axis, or (2) they may move in opposite directions, in which event equality of movement will result in higher crystal symmetry. Modification (1) of a cubic space-lattice, like that of a face-centred space-lattice above dealt with, produces a regular point-system of tetartohedral crystal symmetry; the type of homogeneous structure is No. 2 in Barlow's list. Modification (2), on the other hand, produces a regular point-system possessing pentagonal hemihedry; the homogeneous structure obtained is of type $1a_1$; the unaltered cubic space-lattice is of type $12a_1$.

^{*} See note +, p. 1.

^{† &#}x27;Zeitschr. für Kryst.,' vol. 23, p. 7.

4 Mr. W. Barlow. Interpretation of Indications of

There are also two ways of applying the method to the cube-centred space-lattice. Thus—(a) the points of all four of the component face-centred lattices found lying on a given trigonal axis may be moved in the same direction on this axis; or (b) while the points of two of these component lattices, which together form a cubic space-lattice, found on a given axis are moved in the same direction, this direction may be opposite to that taken by the points of the remaining two found on the same axis. Modification (a) produces, in general, hemimorphic (tetrahedral) hemihedry of the cubic system; the type of homogeneous structure is then No. $2b_1$ in Barlow's list. interesting fact, however, that a particular case of this modification yields holohedral symmetry. Thus, if the shifts of the points along their respective selected trigonal axes bring them to positions midway between the points of the unmodified cube-centred lattice, this highest crystal symmetry results. Modification (b) produces enantiomorphous hemihedry of the cubic system; the type of homogeneous structure is No. 3 or No. 4 in Barlow's list, according to the position of a shifted point on a trigonal axis with respect to the trigonal axes not parallel to this axis.

It is important to observe that additional diversity is achieved if the points of the two compound space-lattices are divided into their component face-centred lattices and the latter then subjected to different amounts of displacement. This inequality of shift of the points results in the production of an assemblage of points consisting of more than one Sohnckian regular point-system, but it is of interest to notice with regard to the cube-centred space-lattice that the shift of a point of one component cubic lattice can be so proportioned to that of a point of the other component cubic lattice lying on the same trigonal axis that the points of the cube-centred lattice become centres of symmetry of the system of shifted points. The two Sohnckian point-systems resulting are then so related as to form one double point-system, viz., a point-system the arrangement of half the points of which bears to that of the other half a mirror-image relation. In this event, instead of the tetartohedral symmetry of type 2, the pentagonal hemihedry of type $2a_1$ is presented. The unaltered cube-centred space-lattice is of type $13a_1$.

Plane diagrams of the above relations are not given here because the details are too involved for them to be useful. Models are needed for showing the three-dimensional properties referred to.

Proposition 2.—The method of modification defined in Proposition 1 makes the points of the space-lattice divisible into four sets, lying respectively on the four sets of differently orientated axes which constitute the selected system of non-intersecting trigonal axes. If, in addition to being equal, the displacements suffered by the points of such a set all have the same direction,

the planes of points found in this set will, it is evident, all present the same orientation and spacing before and after modification.

In the case of the face-centred lattice, the preservation of cubic symmetry requires that the displacements along an axis shall all be in the same direction, while for the other two kinds of space-lattice specified, opposite directions of shift are, as stated, possible for points of the lattice found on the same axis. In all but very exceptional cases, a system of parallel planes of points of one of the four sets just referred to is not congruent with the system of parallel planes having the same orientation of another set; in other words, in the entire system composed of the four sets adjoining spaces between successive parallel planes are neither equal nor present a simple rational relation.]

Proposition 3.—When the space-lattice concerned is regarded as consisting of parallel planes of points, the plane direction of which is perpendicular to one of its four sets of trigonal axes, each of these planes of points (111) is found to be broken up by the process of shifting prescribed into two distinct planes of points; one-fourth of the points of the original plane are shifted to a plane α parallel to it on one side, while the remaining three-fourths are shifted so as to be found in a plane b, also parallel to the original plane, but on the other side of it. The distance of the plane a, containing one-fourth of the points of the original selected plane, from that plane is three times that of the plane b containing the remaining three-fourths of the points.

The following proof is offered:—

Through opposite edges AB, CD (fig. 1, A and B), of one of the cubic elements of a cubic space-lattice draw a plane, and make this the plane of the diagram (B); this plane, besides the four points of the lattice A, B, C, D, contains, when produced, other points similarly situated at the corners of other cubic elements, as shown by the points of intersection of the horizontal and perpendicular lines of the figure.

Let AC be one of the surviving trigonal axes referred to in Proposition 1, and EAF the trace on the plane of the diagram of a plane perpendicular to AC drawn through A, which plane contains other points, such as E and F, of the space-lattice. One-fourth of the surviving trigonal axes, all of which intersect this plane, are perpendicular to it, and have the direction of AC; the remaining three-fourths, which have the other three directions for cube diagonals, all make the same angle with the same plane equal to the angle EAG, made by a diagonal of a cubic element of the space-lattice with the trace EAF.

Let P mark the point on the surviving trigonal axis AC to which the point A of the space-lattice is shifted: all points on trigonal axes parallel to AC originally found in the plane drawn through A perpendicular to AC will, after the shifting, lie in a plane parallel to this plane drawn through P.

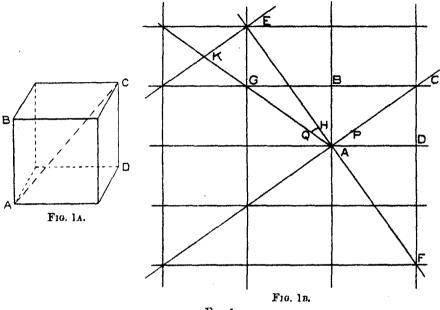


Fig. 1.

The other points of the lattice contained in the plane EAF, which do not lie on the trigonal axes that have the direction AC, lie on trigonal axes having one or other of the three remaining directions for these axes, which directions all make angles equal to the angle EAG with this plane. And, as each of these points also experiences a shift equalling AP along its axis, they all lie in a plane parallel to the plane through EAF, passing through a point Q on the line AG, such that AQ = AP.

Draw QH, EK, both perpendicular to AE; EK is a semi-diagonal of a cubic element.

Since
$$\frac{QH}{AQ} = \frac{EK}{AK}$$
, and $3EK = AK$, it follows that $3QH = AQ = AP$.

Consequently, one-fourth of the points originally found in the plane having the trace EAF are shifted to a plane parallel to this plane, drawn through P at a distance = AP, while the remaining three-fourths are shifted in the opposite direction to a plane also parallel, drawn through point Q at a distance HQ = AP/3.

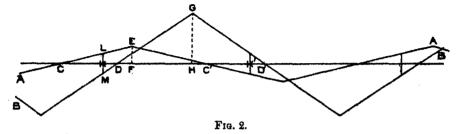
This proof is applicable to any plane (111) of points of either of the three space-lattices possessing cubic symmetry.

Proposition 4.—In the case of a regular system of similar atomic centres which is the outcome of a symmetrical displacement of the kind described, if the intensity of the portion of a given homogeneous (monochromatic) beam of X-rays thrown back at a given angle from a plane of the centres is taken to be proportional to the density with which the plane is beset with these centres, the intensities of two wave-trains travelling in the same direction, derived by similar reflection at the two planes (111) of atomic centres into which a single plane was resolved by the prescribed displacements, will, it is evident, be in the ratio 1:3, for plane b is three times as densely beset as plane a.

Proposition 5.—Since the displacement described converts a single plane (111) of atomic centres into two planes of centres, one of which is found on the one, the other on the other side of the original plane, it is evident that, of the two trains of reflected waves which thus take the place of a single train, one will present an advanced, the other a retarded phase, as compared with that of the single similarly reflected train which would be produced by the same beam falling on the unmodified plane of centres.

Proposition 6.—The phase presented by the resultant of the two wave-trains derived from the beam of X-rays, referred to in Proposition 4, is approximately the same as the phase of the wave-train which would be derived from the same beam by reflection at the unmodified plane of centres. Thus the phase of the resultant of the two reflected wave-trains is approximately constant for different values of the coefficient of displacement of the atomic centres. The following proof of this proposition is submitted:—

The geometrical convention adopted for the representation of waves of propagation of a ray of light consists of a sinuous line, the similar waves of which are of some given wave-length and express the amplitude of the



light waves by their transverse dimensions. In the case of the two reflected wave-trains referred to in Proposition 4, substitute zigzags for sinuous lines, and let zigzag A (fig. 2) represent the wave-train thrown back

from the plane which is less thickly beset with the atomic centres, zigzag B that reflected from the plane which is more so. If the maximum ordinate EF of A is p, GH, which is that of B, will then be 3p.

The superposition of the two wave-trains is expressed by making their median lines coincide in the diagram. The difference in phase is given by the horizontal distance CD measured between nearest median points of the two wave-trains. The median points of the resultant wave-train, at which the ordinates of the component waves cancel each other as being of opposite sign and equal, are marked K, K'.

Since CF = DH, both being a quarter of a wave-length of the beam of X-rays, and 3EF = GH.

Area
$$\Delta$$
*DGH = $\frac{3EF \times CF}{2}$ = 3 area Δ *CEF,

Now
$$\frac{\text{Area }\Delta^{\text{c}}\text{CLK}}{\text{Area }\Delta^{\text{c}}\text{CEF}} = \frac{\text{LK}^2}{\text{EF}^2}$$
, and $\frac{\text{area }\Delta^{\text{c}}\text{DMK}}{\text{area }\Delta^{\text{c}}\text{DGH}} = \frac{\text{MK}^2}{\text{GH}^2} = \frac{\text{LK}^2}{9\,\text{EF}^2}$.

Therefore
$$\frac{\text{area } \Delta^{\bullet}\text{CLK}}{\text{area } \Delta^{\bullet}\text{DMK}} = \frac{\text{LK}^{2} \times \text{area } \Delta^{\bullet}\text{CEF} \times 9}{\text{LK}^{2} \times \text{area } \Delta^{\bullet}\text{DGH}} = \frac{9}{3} = 3.$$

But since LK = KM,

$$\frac{\text{Area } \Delta^{\circ}\text{CLK}}{\text{Area } \Delta^{\circ}\text{DMK}} = \frac{\text{CK}}{\text{KD}}; \text{ therefore } \text{CK} = 3 \text{KD}.$$

Now the difference in phase of the portion of a given wave-train reflected which would be produced by shifting the reflecting surface while maintaining its original plane direction is proportional to the amount of shift, i.e., to the distance through which this surface is moved along a normal. Therefore if the difference in phase between the portion of the incident beam which would be reflected from the original plane and that reflected from α be m, the difference in phase between the former and that reflected from b will be m/3. Therefore, since CK = 3KD, the point K marks a median point of the wave-train reflected from the original plane of centres corresponding to the median points of the trains A and B marked respectively C and D. In other words the wave-train which is the resultant of these two wavetrains is in the same phase as the wave-train which would be produced by reflection of the given beam of X-rays at the unmodified plane. similarity of the phases referred to would therefore be established not merely approximately but absolutely if the wave-trains were correctly represented by the zigzags of the diagram. If sinuous line waves are needed for the correct representation of the waves of X-rays concerned, and these line waves approximate more or less in form to the zigzags depicted, the relation deduced above will more or less approximately obtain, but not exactly.

Fig. 2 is drawn showing the difference of phase CD less than a quarter wave-length CF; the reasoning equally applies if it is shown greater.

Proposition 7.—A similar argument to that given above in respect of planes of centres (111), and found applicable to all the four sets of these planes, is available for the three sets of planes (100) and the six sets of planes (110). The reasoning employed for these will, however, be rather simpler than that given above in regard to planes (111), because the density of the distribution of the centres in the shifted planes is, for the plane directions (100) and (110) found to be equal in the two derived planes.

[Added July 20: Proposition 8.—In all regular point-systems the arrangement of which is derived from one or other of the three space-lattices referred to by the method of modification described, every set of parallel equidistant planes of points presents an orientation and spacing of its consecutive planes strictly the same as those of the corresponding set of parallel planes of the lattice.

This is an immediate consequence of the equality of the shifts to which the points are subjected, and of these shifts forming sets, each of which has its own uniform direction.

Proposition 9.—The characteristic symmetrical distribution of X-ray intensity observed when homogeneous (monochromatic) X-rays are passed into a crystal of a simple compound belonging to the cubic system does not suffice to determine at all precisely the nature of the arrangement of the atoms. There is definite evidence of the existence of a precise dimensional relation between the wave-length of the X-rays employed and the actual magnitudes of the intervals separating successive planes of atomic centres in various directions, but this evidence does not suffice to show whether the atomic arrangement actually prevailing in the crystal is the space-lattice one compatible with the particular spacing of these planes indicated in the crystal under observation, or that of one of the innumerable various point-systems of cubic symmetry derivable from this space-lattice by the method described.

The following proof is submitted:-

The theory of the action of crystals on homogeneous (monochromatic) X-rays recently arrived at by W. H. Bragg and W. L. Bragg, suggested by their new experimental methods, may be shortly stated thus:—

1. The planes of atomic centres distinguishable in the regular systems according to which the homogeneous structures known as crystals are arranged, function as reflecting surfaces when impinged upon by a beam of X-rays.

- 2. Since every kind of plane of atomic centres present is repeated at uniform intervals so as to constitute a system of equidistant parallel planes, the phenomenon is over and over again presented of the beam falling on a series of parallel equally spaced reflecting surfaces, each of which acting alone can reflect but an imperceptible fraction of the incident radiation.
- 3. Reflection is thus more or less feeble unless the angle of incidence is such that the difference of phase of the portions of the beam reflected at the successive equidistant planes of such a series is congruent or very nearly congruent with the wave-length; in other words, unless the waves of the reflected wave-trains coincide and so reinforce one another. The familiar equation $n\lambda = 2d \sin \theta$ gives the glancing angles at which the intensity of the resultant reflected wave-train is a maximum; λ is the wave-length of the rays employed, θ the glancing angle of reflection, d the distance between the successive planes of the series of equidistant planes, and n a whole number. Thus reflection has maximum intensity at a series of angles θ_1 , θ_3 , θ_3 , etc., the sines of which are in an arithmetical progression obtained by substituting integers 1, 2, 3, etc., for n.

The reader is reminded that any series of equidistant planes of atomic centres will commonly be intercalated with one or more similarly spaced series of planes of centres of the like orientation, the distance separating a plane of one series from a plane of another not, however, presenting a rational relation to the appropriate value of d.

- 4. A study of the comparative intensities of the first, second, third, and higher orders of spectra obtained from the variously orientated sets of planes leads to the discovery of the simplest scheme of atomic arrangement which would give comparative intensities for the different maxima in agreement with observation. The analysis is carried out by combining, mathematically, the waves of length λ reflected in the same direction from the various sets of planes, assigning to each wave an amplitude proportional to the mass per unit area of the plane which reflects it. By a process of trial and error an atomic arrangement is arrived at which would account for the observed intensities.
- 5. The various distances d for the differently orientated series of equidistant planes are calculated from the density of the crystal, the molecular weight of the unit of the crystal pattern and the comparative dimensions of the scheme of arrangement referred to in 4.

Now, as will have been seen from the foregoing, the regular point-systems derivable as explained fall into two classes, viz.:—

(a) Those in which the direction of displacement is the same for all points of the lattice found lying on the same trigonal axis.

(b) Those in which the points of the lattice found on a trigonal axis are some of them displaced in the one direction along this axis, the rest in the opposite direction.

All the cases of the modification of the face-centred space-lattice belong to class (a) (see p. 3).

Following the lines of this division into two classes a difference in the rigidity of the proof of Proposition 9 has to be noted. In cases of class (a) the proof is absolute; the difference in phase of the similar reflected wavetrains following a given direction produced by successive reflections at a number of parallel planes is precisely the same in the space-lattice arrangement as in any one of the point-system arrangements derived from this space-lattice by the defined method; and this is true whatever the direction chosen. This immediately follows from Proposition 8. For when the effect on the X-rays of a derived regular point-system is compared with that of the parent space-lattice and attention is confined to cases of class (a) it is clear that the break up of each plane of points of the spacelattice into two planes of points parallel to it (see Proposition 3) gives two component sets of reflected wave-trains in any given direction in place of each single set thrown back by the equally spaced parallel planes of a certain orientation of the space-lattice; and since each such component set presents the same phase difference as that characterising the corresponding set of the space-lattice, this phase difference will also be presented by the resultant set produced by the coalescence of the component sets referred to. Proposition 9 is therefore established for all cases of class (a), and it is clear that this conclusion is not affected by any question of the degree of accuracy attainable in the observations; the molecular weight of the unit of the crystal pattern is not affected by the modification contemplated, and although the number of distinct sets of parallel planes of centres is increased, the values d remain unchanged. However near precision the estimation of the results of the X-ray investigation may be, the argument based on them will therefore, in cases of class (a), fail to indicate which of the alternative atomic arrangements is the one actually prevailing; some additional fact is needed for determining this.

The proof of Proposition 9 for cases of class (b) rests on that of Proposition 6, which admittedly deals with approximations. This raises the question whether the quantitative results obtained experimentally are sufficiently precise to render even a very slight departure from the ideal distribution of intensity in the different directions adequate to rule out the solutions which involve this discrepancy. It is submitted that the degree of experimental refinement reached will not suffice for this. And, on the

other hand, very important considerations will be brought forward to show that in one particular instance a point-system arrangement, which differs profoundly from the space-lattice from which it is derived, manifests a much closer agreement with the experimental facts than this space-lattice does.

In comparing two kinds of atomic arrangement for the purpose of Proposition 9, the assemblages of atoms employed are taken to be similarly orientated; in other words they have corresponding axes parallel.

It follows directly from Propositions 6 and 8 that the phase-difference of successive reflected wave-trains following any given direction with respect to the axes is the same, within experimental error, for a space-lattice arrangement as for any point-system derived from this space-lattice by the method described. And the correspondence of the phase-differences for the same direction in two different arrangements carries with it similarity of the disposition of the directions of maximum intensity in any two assemblages related in the manner defined. Thus Proposition 9 is established to the degree of approximation afforded by Proposition 6. Additional data are therefore required for discovering the arrangement of the atoms in the molecule, and, indeed, for determining the nature of their distribution in space.

The particular case to which allusion has just been made will now be taken:—

W. L. Bragg has concluded* that the atoms of sodium and chlorine in the crystal of common salt NaCl very approximately occupy the points of a cubic space-lattice; the two component face-centred lattices of which the cubic lattice is made up (p. 2) mark respectively the suggested disposition of the two different kinds of atoms.

The need for some modification of this view is suggested by the fact that the arrangement reached does not lend itself to a distribution of the centres of the chemical molecules in harmony with the crystal symmetry. If the centres of the molecules NaCl are supposed to lie about half-way between nearest atom centres of the two kinds, the most symmetrical disposition possible for the molecular centres gives tetragonal symmetry; cubic symmetry is not attainable. Consequently, if molecules exist as individuals in the crystalline condition, such an arrangement must be out of harmony with the crystal form.

No such difficulty presents itself if the arrangement of the atoms is one derived from the cubic space-lattice by a certain application of the method of modification described. For let one-fourth of the trigonal axes of the cubic space-lattice be selected so as to furnish a cubic system of non-

^{* &#}x27;Roy. Soc. Proc.,' A, vol. 89, p. 469.

intersecting trigonal axes (p. 1): the two kinds of atoms are, according to Bragg's view, found placed alternately on each selected trigonal axis so that each atom lies midway, or about midway, between two atoms of the other kind present on the selected axis. Let, now, all the atoms of one kind present on one of the selected axes be moved uniformly towards one end of this axis, and all the atoms of the other kind found on this axis, to the same extent, towards the opposite end, neither kind of atom leaving the axis, and let the amount of displacement be such that the distance apart of the atoms of two kinds which have thus approached is slightly under the distance originally separating two nearest atoms. Let the atoms of two kinds which have approached be taken to form a molecule; all the molecules NaCl found on the axis taken are then similarly orientated. The carrying out of the coincidence-rotations about the axes of the system of non-intersecting trigonal axes will locate a similar atom arrangement on all the remaining trigonal axes and give an assemblage in accordance with the cubic symmetry of the system of axes. The centres of the molecules, if taken to lie midway between the centres of their atoms, are found arranged to form a facecentred lattice, although, in consequence of variety of orientation of the molecules, the assemblage does not present the high symmetry of this lattice.

A model of this scheme can be constructed to show both the symmetry of form of the polyhedral cell, which represents the domain of predominant influence of a single atom, and also the arrangement of the atoms and of the centres of the molecules. The following is the method of construction:—

Take a number of hollow indiarubber balls of the same size, and form pairs by sticking them together two and two; each pair is to represent a molecule. Arrange the points of contact, which are the centres of the pairs, to form a face-centred space-lattice, viz., as the sphere centres of a cubic closest-packed arrangement of equal spheres. Next, keeping the centres of the pairs in the relative situations prescribed, arrange the axes of the pairs symmetrically in four different orientations in harmony with the coincidence-movements of a set of non-intersecting trigonal axes. Finally, while preserving the relative arrangement of centres and axes thus reached, uniformly compress the mass so as to bring the pairs of balls together and flatten them at places of contact till all the interspaces are practically eliminated. In the resulting assemblage each ball centre is found nearly equidistant from 13 ball centres immediately surrounding it, and consequently each of the similar space-filling polyhedral cells producible by the process has 13 faces and is nearly capable of being circumscribed about a sphere. Thus the scheme reached immediately suggests stable equilibrium.

14 Mr. W. Barlow. Interpretation of Indications of

Since the atoms are of two kinds, but of the same fundamental valency, it is suggested that balls of two slightly different sizes may be used to represent the two kinds of atoms. The special relation of each atom to the one next to it with which it is chemically united to form a molecule suggests a shortening of the distance between each ball centre and the centre of the ball nearest to it on the same trigonal axis; the centre of the larger polyhedral face thus produced will practically coincide with the centre of the molecular group of two atoms.

It is clear from the foregoing that, while the scheme of arrangement suggested is in harmony with the X-ray results, it is in three respects in better agreement with the facts than the cubic space-lattice arrangement is. Thus:

(1) The centres of the molecules are arranged according to cubic symmetry a condition impossible for the unaltered arrangement of the cubic space-lattice. (2) The symmetry indicated is not, like that of this lattice, holohedral, but is hemihedral, as are the actual crystals.* (3) Stable equilibrium is indicated by the relation of each centre to the centres immediately surrounding it.

In the model just described the distance apart of the centres of two balls representing the two atoms of the same molecule differs but little from that separating the centres of adjoining balls not thus related. It is, however, an interesting question whether the experimental facts are consistent with a much closer drawing together of the centres of the two related atoms, such that their distance apart becomes quite small compared with the distance separating nearest centres of the chemical molecules. The unit composed of two polyhedral cells, which represents the domain of predominant influence of a single molecule, would in such a case appear to approximate to sphericity and the enquiry arises whether this is possible without making the degree of approximation contemplated by Propositions 6 and 9 fall below the limit of experimental error of the X-ray methods.]

Proposition 10.—Inasmuch as every arrangement of points which displays cubic symmetry can be uniformly distorted to produce corresponding dispositions of the points exhibiting the kinds of symmetry of most of the other crystalline systems, and in this process the dimensional proportions in any given direction are preserved, it follows that, so far as geometrical possibilities are concerned, a very similar method of modification to that above described can be applied to all kinds of space-lattice arrangements of atoms of whatever symmetry, so as to produce from them point-systems

^{*} The hemihedry of NaCl is not so clearly indicated as that of some of the allied halogen compounds KCl, KBr, etc., to which the arguments here given also apply.

which produce an effect on X-rays practically indistinguishable from that produced by the unmodified space-lattice arrangements respectively concerned.

It is therefore a general conclusion that the nature of the spacing of the parallel planes of atomic centres, as revealed by the results of the application of X-rays to crystals obtained by Laue and by W. H. Bragg and W. L. Bragg, is not so unambiguously indicated as at first appeared. For practical purposes these results are in many cases in harmony not only with the existence of very simple arrangements of the atoms according to an elementary space-lattice or combination of space-lattices, but are also equally consistent with a less symmetrical kind of arrangement derived by a considerable modification of the space-lattice or space-lattices, which leaves the system of crystal symmetry presented the same as before the alteration, but lowers the class. The fact that hemihedry is in so many cases presented by the crystals of simple compounds may be regarded as an indication that the actual arrangement of the atoms is of the less symmetrical kind.

But while insisting on the importance of ascertaining precisely the ambit of the new X-ray method of analysis of crystal structure, the author fully recognises that this method, as applied by W. H. Bragg and W. L. Bragg, is the basis on which the above conclusions rest; his argument, if sound, is an additional testimony to the value of this singularly beautiful form of research. And the admission that we are not so near to finality as at first appeared will make it more, not less, important to carry on the work. When in a given case the limits between which a solution must be sought have been found by the method, the student will doubtless be stimulated to examine the distinctive features of this case by all the means available, in order to find the additional factor needed for an exact determination.

A word in closing as to the bearing of the above conclusion on the work that has during the last few years been done in the investigation of atom arrangements from the standpoints of the chemist and crystallographer; this is largely based on observations of relative axial dimensions of crystals of allied substances, and on evidence as to the constancy of the proportionate volumes appropriated by the individual atoms, which is interpreted as indicating the existence of what is termed the law of valency volumes. In view of the above conclusions one is tempted to enquire whether it will not be possible in all cases to indicate an arrangement for the atoms of a crystal which is at the same time consistent with the results of an X-ray investigation and compatible with the conception that stable equilibrium is very approximately represented by a close packing of spheres of appropriate sizes, each of which stands for a single atom, variety of

pattern being attributed to modification of the spacing due to the presence of links which attach atom to atom to form certain groups or molecules and also to differences in magnitude of the atomic domains. coincidence between chemical theory and a conclusion reached by means of the X-ray method of investigation gives pause, however. The arrangements which chemists assign in their graphic formulæ to the carbon atoms in the principal typical carbohydrates are precisely such as are presented by appropriate fractions of the point-system which Bragg has deduced as giving the arrangement of the carbon atoms in a crystal of diamond*; it is seen on examination that, so far as comparison is possible, precisely the same tetrahedral environment of each carbon atom is presented in both cases. Is it possible then that a tetrahedral group of four spheres in close contact forms a correct graphic representation of the four unit valency volumes of a carbon atom, and that a fitting of these tetrahedral groups closely together, which gives a distribution of their centres identical with that of Bragg's diamond structure, the correctly gives both the structure of this crystal and that of strings or chains of carbon atoms as they actually occur in the carbon compounds? The prospect seems inviting, but additional facts are needed to establish or modify such a conception, and to ascertain whether and how far it applies to other atoms than those which enter into the composition of organic compounds.

^{* &#}x27;Roy. Soc. Proc.,' A, vol. 89, p. 277.

[†] Cf. 'Scien, Proc. Roy. Dublin Soc.,' vol. 8, p. 542.

The Ignition of Gases by Condenser Discharge Sparks.

By Prof. W. M. THORNTON, D.Sc., D.Eng., Armstrong College,

Newcastle-on-Tyne.

(Communicated by the Hon. Sir Charles Parsons, F.R.S. Received June 29, 1914.)

1. It may be taken as an axiom of electrical ignition that the closer its conditions resemble those in the explosion wave front the more readily will it occur. These conditions are high temperature and pressure, and in the case of hydrocarbons combustion to carbon monoxide. They are also characteristic of condenser discharge sparks, for in the first place the surface of a platinum pole to which condenser discharge has been made becomes pitted to a remarkable extent, greater than when large currents are broken by separation of the poles. The sparks have therefore a high temperature. That they give rise to high gas pressure is clear from the intensity of the sound of a single spark discharge, and finally it will be shown that combustion to carbon monoxide rather than to carbon dioxide is peculiar in certain cases to ignition by capacity sparks. In addition to these the sparks are of very short duration, are oscillatory in character, and start with ionisation or breakdown of the gas between the poles. The belief that all visible

sparks will ignite explosive mixtures no doubt arose from observations of the activity of condenser discharge in this respect, but while in certain cases, especially in the ignition of hydrogen, the least igniting sparks are very small, yet there is in every case a well marked limit to their igniting power, and as the percentage of gas limits of inflammability are approached they require to be large.

2. The Paraffins—Ethanc, Propane, and Butane.—The gases used in the present work were from the same stocks as those used for break-spark ignition.* The results obtained from them are given in fig. 1. They have

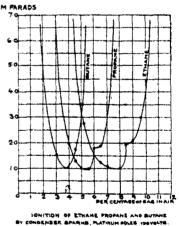


Fig. 1

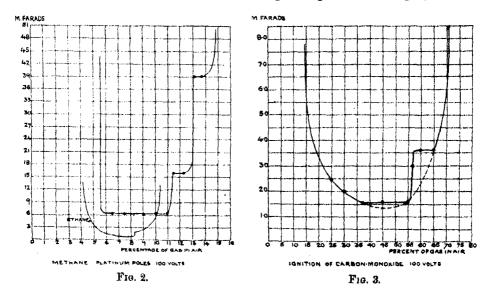
two interesting features; their minimum igniting current is the same in every case, in this resembling their ignition by continuous current break-

^{* &}quot;The Electrical Ignition of Gaseous Mixtures," W. M. Thornton, 'Roy. Soc. Proc.,' A, vol. 90, p. 272 (1914).

sparks, but they have the parabolic form characteristic of alternating current break-spark ignition. Ethane has, however, a minimum at 7.7 per cent., the point of combustion to carbon monoxide, the others, as before, midway between this and combustion to carbon dioxide. There is, however, on the higher side of the ethane and propane curves—the supply of butane gave out before this could be examined fully—a step or increase in difficulty of ignition corresponding to mixtures midway between four and five atoms of oxygen to one molecule of ethane, and between six and seven to one of propane. This point was thought to be some failure in the quality of the gas, but when it appeared in both, and to a still greater extent in methane, it was more fully examined. Condenser-spark ignition has therefore some of the features of both continuous and low frequency alternating current break-spark ignition, but it has a characteristic type of its own.

It may be remarked in passing that the energy per atom in unit volume of each of the three gases at the minimum of each curve is the same, in this resembling break-spark ignition.

3. Methane.—From the previous work it was expected that methane would have the same minimum as ethane, propane, and butane, but this was found to be not the case, and after several samples of pure methane, prepared at



different times, had been very kindly sent to me by Dr. Wheeler for examination, the conclusion was reached that the mode of ignition of methane by condenser sparks was of an entirely new type, as shown in fig. 2. In the first place the energy required to obtain any ignition at all

was much greater than in the other paraffins; 6.5 microfarads had to be used at 100 volts as compared with 1 microfarad in the heavier gases. No ignition could be obtained below 6.25 per cent.; from this to 10.5 per cent. the energy of the least igniting spark was the same, but at 11.5 per cent. the necessary energy suddenly increased, so that nothing less than 16 microfarads would give an igniting spark. The mixture giving combustion to CO₂ had been passed through without change; combustion to CO is at 12 per cent. At 13 and 13.5 per cent. 40 microfarads had to be used, and above this no ignition could be obtained by condenser sparks with all the available capacity of 46 microfarads in use. The sparks were then of great brightness and pitted the poles freely. The stages may be more readily followed by a comparison of fig. 2 and Table I. The critical steps are at 11.5 and 13 per cent.

Table I.

Mixture.	Percentage of gas in air
2CH ₄ +O ₈	9.36
$2CH_4 + O_7$	10.5
$2CH_4 + O_6$	12.0
$2CH_4 + O_5$	15.0

When the oxygen atoms are more in number than those of the combustible gas each stage appears to be symmetrical on either side of one of the critical percentages, when they are equal or less in number the step coincides with the critical percentage as in carbon monoxide and hydrogen. Numerical excess of oxygen therefore retards the rise of difficulty of ignition as much as possible, that is, half a stage.

4. Carbon Monoxide.—In order to see whether the ignition by steps occurred in other gases having a single carbon atom, carbon monoxide was examined (fig. 3). The figure is interesting on account of the well marked transition of stages. In the first from the lower limit to 37.5 per cent. the curve has the parabolic form. The mixture for complete combustion to CO₂ is at 29.2 per cent. and this is now passed through without notice, though with the break-sparks there is a change of type approaching 30 per cent. At 37.5 per cent. a new stage is entered, from 37.5 to 56 per cent. the same igniting energy is required and the curve is horizontal. This clearly corresponds to an increase in difficulty of ignition, for the usual alternating current curve would fall below it. Above 65 per cent. the limit is rapidly approached,

and at 70 per cent. 28 microfarads are required for ignition. The meaning of the steps can be seen in Table II.

Table II.

Mixture.	Percentage of gas in air.
2CO + O ₂	29 ·2
$3CO + O_2$	38 · 2
$4CO + O_2$	45.1
6CO + O ₂	55 -2
9CO + O ₉	65.0
$12CO + O_2$	70.6

In this case there is an increase in difficulty of ignition as the combustible gas increases in multiples of 3.

5. Hydrogen Sulphide.—That these several steps are not peculiar to gases with single carbon atoms is shown by the behaviour of hydrogen sulphide (fig. 4). The gas was not specially purified and probably contained 1 per cent. of hydrogen; its limits of inflammability were observed to be at about 4.8 and 20 per cent. The steps occurred at 10 and 14 per cent., the mixtures being as in Table III.

Table III.

Mixture.	Percentage of gas in air.
H ₂ S + O ₃	17 · 1
H ₂ S + O ₄	12 · 0
H ₂ S + O ₆	7 · 6

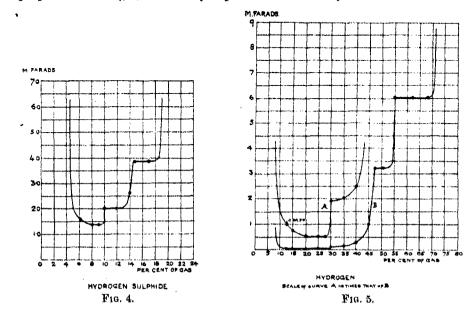
Here the oxygen atoms are more in number than those of the combustible gas and these percentages are intermediate between the rising lines.

6. Hydrogen.—The ignition of hydrogen exhibits the stages very well, as shown in fig. 5. The observed steps are at 30, 45, 55, and 70 per cent., the upper limit being 72 per cent. As shown by Table IV the hydrogen atoms are more in number than the oxygen and the steps are at the critical mixtures.

Table IV.

Stage.	Mixture.	Percentage of gas in air.	
1	H ₂ + O	29.2	
2	2H2+O	45.2	
8	8H,+O	55 .2	
1	4H ₂ +0	62 ·2	
1	5H ₂ +O	67 .4	
4	6H ₂ +O	71.2	

The coincidence between the mixtures with 1, 2, 3 and 6 hydrogen molecules to one oxygen atom and the observed steps are very close, and there cannot be any doubt that with certain gases of simple composition the play of forces upon an oxygen atom in the act of ignition can be observed in this way. The occurrence of ignition by steps has little or no relation to the other properties of the gas, and it may depend almost entirely on structure.



7. Cause of Stepped Ignition.—The strongest argument that each rise in the curves is an increase in difficulty of ignition over that which would have normally been found in a purely thermal reaction is in the behaviour of methane. Here the first stage begins immediately after the lower limit. If there had been a gradual fall from this as in carbon monoxide or in the higher paraffins, it would by analogy with all previous results have reached the same level as ethane. The occurrence of a horizontal stage is not peculiar to condenser ignition, for it has been observed in the ignition of hydrogen and of carbon monoxide by break-sparks,* and in these cases also it indicated that more energy was required than if the rounded curve had been followed. In the present case the carbon monoxide curve presents the clearest evidence of the nature of the transition.

The cause of this increased resistance is probably that when an atom of combustible gas—or of oxygen in some cases—is surrounded by molecules with one or more of which it is eventually to combine, the difficulty of

choice of any single partner is increased by the simultaneous attraction of the others, and more energy must be given to the gas to set up a movement so violent that any pair is forced into "contact." In some cases, carbon monoxide for example, the difficulty of ignition only becomes acute in certain aggregates, thus the steps are at 3, 6, and 9 molecules of carbon monoxide to 1 of oxygen. In methane it is when there are 3 or 4 molecules of oxygen to 1 of methane. In hydrogen the critical ratios of hydrogen, molecules to oxygen atoms are 1, 2, 3, and 6.

8. Absolute Energy of Ignition.—With carbon monoxide the energies of the two stages are 0.0082 and 0.018 joules, a ratio of 1 to 2.19, and there are twice as many molecules of CO in the second case. In methane the energies of the stages are 0.032, 0.8, 2 joules, in ratios 1:2.5:6.25. In hydrogen sulphide the energies are 0.007, 0.01, 0.0195, in ratios 1:1.43:2.79. In hydrogen the energies and ratios are as in Table V.

Table V.

Stage.	Energy of spark in joules.	Ratios.	
1	0 .00025	1	
2	0 .00095	8.8	8.8
3	0.0016	6 4	1 .7
4	0.0080	12 .0	1 .87
		Mean	2 ·1

It would appear that the ratios of the energies in successive stages increase very approximately in a constant ratio 2, so that the difficulty of ignition is on an average doubled at each step. This is the more remarkable since the number of molecules in contact with a combining atom is not as a rule doubled. With more complex molecules the arrangement of atoms in the molecule will probably influence the relative ease of ignition.

On the Fluorescence of Iodine Vapour Excited by Ultra-Violet Light.

By Prof. J. C. McLennan, University of Toronto.

(Communicated by Prof. A. Schuster, Sec. R.S. Received June 24,—Read June 25, 1914.)

[PLATE 1.]

I. Introduction.

In a recent communication* by the writer a new fluorescence spectrum of iodine vapour was described which could be stimulated by the light from the mercury arc. This fluorescence spectrum consisted of a set of narrow bands extending from λ 4600 down to λ 2100. While the whole of this spectrum was clearly defined, the most intensely marked portion of it was made up of a set of seven equally spaced bands between λ 3315 and λ 3175. In obtaining the spectrum a highly exhausted tube of fused quartz containing a few iodine crystals was inserted axially in an ordinary glass Cooper-Hewitt mercury arc lamp, with a lateral anode and provided with a short extension at the positive end, to which the quartz tube was sealed with mastic wax. The quartz iodine vapour tube was provided with a window of clear fused quartz, towards which the collimator of a quartz spectrograph was directed in taking the photographs. When the Cooper-Hewitt tube was in action the arc played directly upon the inserted quartz tube and so subjected the vapour contained in it to intense illumination.

In the paper describing this fluorescence spectrum of iodine vapour it was pointed out that it was impossible to obtain the spectrum when the inserted tube containing the iodine vapour was made of combustion glass tubing. It was also pointed out that this glass tubing was found to be transparent to the light from the mercury are down to λ 2893.7, and on account of this fact the conclusion was drawn that the light which stimulated the iodine vapour to the fluorescence referred to must have had a shorter wave-length than λ 2893.7.

The present communication contains the results of experiments made to determine the range of the exciting light, together with a statement of some points of interest in connection with the fluorescence spectrum which developed while these experiments were being made.

^{* &#}x27;Roy. Soc. Proc.,' A, vol. 88, p. 289 (1913).

II. The Effect of Temperature.

In order to ascertain, approximately at least, the temperature at which the iodine vapour was maintained when it emitted the fluorescence spectrum with the experimental arrangements described above, the projecting end of the quartz tube containing the vapour was cut off and one of the terminals of a nickel-iron thermo-couple was inserted. When the Cooper-Hewitt lamp was put into action this terminal was shoved along in the tube to different positions and the thermo-electromotive force developed at each position was noted. The details of this investigation have been described elsewhere but the chief point of interest here is that at all points along the tube where the latter was directly in contact with the arc it was found that under the conditions of the experiment the temperature was always within two or three degrees of 326° C.

This explains the absence from the plates of any trace of the resonance spectra which, as Wood has so beautifully shown, iodine vapour emits when the light of the yellow and green lines of the mercury arc is allowed to fall upon it; for in a communication from him to the writer he states that such resonance spectra are no longer emitted when the vapour is raised to a moderately high temperature.

Further experiments showed that iodine vapour could be made to emit its fluorescence spectrum under stimulation by the light from the mercury arc at room temperatures as well as at the temperature 326° C. To show this, some iodine crystals were placed in a tube of clear fused quartz 3.5 cm. in diameter and about 60 cm. in length. The tube was then placed alongside of a Cooper-Hewitt mercury are lamp, also made of fused quartz. When this lamp was put into action, and the light emitted by the iodine tube through one of its ends examined with a quartz spectrograph, it was found to give both Wood's resonance spectra and the fluorescence spectrum described by the writer. With a set of lighted Bunsen burners placed beneath the iodine tube, and the latter raised to a red heat, the resonance spectra once more disappeared from the photographs, but the fluorescence spectrum remained, with no apparent diminution in intensity. It was therefore evident that, while the resonance spectra could only be obtained at comparatively low temperatures, the fluorescence spectrum could be obtained from the iodine vapour over the whole range of temperatures from that of the room up to about 1000° C.

[&]quot; 'Roy. Soc. Canada Proc.,' May, 1913.

III. Excitation Region.

In attempting to locate the range of wave-lengths of the light which stimulated the iodine vapour to fluorescence, the apparatus shown in fig. 1 (Plate 1) was used. AB was an inner tube of fused quartz and CD an outer one of the same material. The diameter of the inner tube was about 2 cm., and the space between the inner and the outer tube was about 5 mm. The inner tube, which was highly exhausted, contained the iodine vapour. When this double tube was placed alongside of the quartz Cooper-Hewitt mercury lamp in action, it was found that the iodine was stimulated to fluorescence when the space between the two tubes was filled with air or oxygen at atmospheric pressure or with distilled water, but not when it was filled with glycerine. With the latter substance, however, the spectrograms showed that light down as far as $\lambda 2340$ entered the iodine tube. The light which stimulated the iodine to fluorescence must therefore have been of a still shorter wave-length than λ 2340. In seeking for a lower limit to the region of excitation, it was not found possible to determine it very definitely. Layers of fused quartz and of water, each 5 mm. in thickness, were both found to be still transparent to light as short as λ 1849 in wave-length. Lyman* has shown that crystal quartz is not transparent to light of shorter wave-length than λ 1600, and it is probable that this may be taken as the limit of transparency for fused quartz as well.

Lyman† has also shown that air at atmospheric pressure has a strong and wide absorption band beginning at λ 1710, and oxygen, at the same pressure, a band beginning at λ 1760. As there was always an air space between the lamp and the iodine tube of from 3 to 4 cm., it is clear that the light which caused the fluorescence must have been of longer wave-length than λ 1760. The experiments described so far, therefore, show that the excitation region lay between λ 2340 and λ 1760. As the strong lines in the mercury are spectrum in this region are given by Handke‡ and by Wolff§ as λ 1942·3 and λ 1849·6, it appeared that the fluorescence was excited by the light of one or both of these lines.

To test the matter still further, a series of photographs was taken with a small quartz spectroscope, with its slit close to the quartz mercury lamp. In all these photographs the line λ 1942.3 came out quite clearly, but no trace of the line λ 1849.6 was obtained. This, as Kirschbaum's

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* Lyman, 'Astrophys. Journ.,' vol. 25, No. 1, p. 45 (Jan., 1907).
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[†] Lyman, 'Astrophys. Journ.,' vol. 27, No. 3, p. 87 (March, 1905).

[#] Handke, 'Untersuch. im Geb. der Schumannstrahlen,' Berl., Diss., 1909.

[§] Wolff, 'Ann. der Phys.,' vol. 42, p. 825 (1913).

^{||} Kirschbaum, 'Electrician,' vol. 72, p. 1074 (1914).

later experiments have shown, was due to the fact that the light of this wave-length is strongly absorbed by mercury vapour. The comparatively cool layers of mercury vapour in the lamp close to its walls, therefore, must have acted as an absorbing screen, and so prevented the light of that wave-length from getting out of the lamp tube with sufficient intensity to affect the photographic plates. From these experiments it would appear, then, that the light from the mercury are which stimulated the iodine to fluorescence was chiefly that of wave-length λ 1942.3.

Further experiments were made which showed that the fluorescence of iodine vapour could be excited by light from the mercury spark in air as well as by that from the mercury arc. In these, two tubes of ordinary silica tubing were sealed into two iron cups, and were then fastened to a support, with their lower ends some distance apart and with their upper ones close together. The tubes were filled with mercury and the iron cups were connected to the two terminals of an induction coil with two halfgallon Leyden jars in parallel. In spectrograms taken with this form of mercury spark, the line $\lambda 1849.6$ came out quite clearly, and the line $\lambda 1942.3$ was much stronger than it was on the plates taken with the mercury arc.

With the mercury spark placed close to the iodine tube, it was found that the fluorescence was considerably stronger than it was when the mercury are was used to stimulate the vapour.

After it was found that fluorescence could be excited in the iodine vapour by the light from the mercury spark, the light from the spark between terminals of a number of other metals was tried. These included aluminium, zinc, cadmium, and magnesium, and with all of them it was found that strong fluorescence was excited. This made it clear that it was not necessary for the exciting light to be of one definite wave-length, and that it sufficed if the light was confined to a portion of the spectrum lying somewhere near λ 1942 and between λ 2340 and λ 1760.

In order to determine within narrower limits if possible the excitation range of wave-lengths, some additional experiments were made with the tube shown in fig. 1, in which mixtures in different proportions of glycerine and water were used as absorbing screens. When a screen of 5 parts water to 1 of glycerine was used it allowed the light from the zinc spark corresponding to $\lambda 2063$ to enter the iodine tube, but cut off the line $\lambda 2026$ and all below it. With an aluminium spark this screen also cut off the light corresponding to the strong line $\lambda 1990$, as well as all light from that source of still shorter wave-length. However, when this 1 to 5 glycerine-water screen was used and the light from the aluminium, the

zine, the cadmium, or the mercury spark was allowed to fall upon the tube, it was found that the fluorescence spectrum always came out, though very faintly, on the plates. In these experiments the exciting light must have belonged to wave-lengths between λ 2340 and λ 2063, and as the fluorescence obtained under these circumstances was faint, it would go to show that the excitation range of wave-lengths began somewhere near λ 2100. It was found impossible with the resources available to ascertain with any exactness the lower limit to the excitation region, but it may be of interest to point out that although the iodine vapour was exposed for 26 hours to the γ -rays from 30 mgrm. of pure radium bromide, and also later for two hours to the strongest Röntgen rays, no photographic indication of fluorescence was obtained.

From the fact that very strong fluorescence was obtained with light from the aluminium and mercury sparks, and the fact that the spectra of these metals both include a strong line between $\lambda 1900$ and $\lambda 2000$, it would seem that the maximum of the excitation range of wave-lengths was somewhere between these limits.

As the bands constituting this fluorescence spectrum began at about $\lambda\,4600$ and were detectable down to about $\lambda\,2100$ it would seem from what has gone before that we have to do here with a case of ordinary fluorescence where Stokes' law is followed and where fluorescence is stimulated by the light from any one of a number of wave-lengths of a limited portion of the spectrum.

Further, it is clear that this ultra-violet fluorescence spectrum of iodine vapour is entirely different in its characteristics from the resonance spectra obtained by Wood with iodine vapour, for (as he has shown) the constitution of each of these resonance spectra is determined by and depends solely upon exciting light of a single wave-length.

IV. Fluorescence of the Vapours of Iodine Compounds.

When working with the original form of apparatus in which the iodine tube was inserted axially in a Cooper-Héwitt lamp and exposed directly to the light of the mercury arc, experiments were made to see if the vapours of a number of the compounds of iodine could be stimulated to fluorescence. None was obtained with zinc, bismuth, or phosphoric iodide, but with both iodoform and mercuric iodide a fluorescence spectrum was obtained which contained the seven well-marked bands of the iodine vapour fluorescence spectrum between λ 3315 and λ 3175.

The fluorescence spectrum of mercuric iodide, however, differed from that of iodine vapour in that it possessed some special characteristics of its own.

It contained a set of five narrow well marked bands or lines between λ 3130 and λ 3020, a set of fine lines, less well marked, between λ 3020 and λ 2923, and also a set of fine lines extending from λ 4359 to λ 3660. It contained besides two broad fluorescent bands with their centres approximately at λ 3440 and λ 3280 respectively. In addition to the seven well marked lines of the iodine vapour fluorescence spectrum referred to above, the fluorescence spectrum of iodoform also contained the bands of the iodine fluorescence spectrum between λ 4290 and λ 3625, but no others. The fluorescence spectrum of iodoform differed from that of mercuric iodide in that it did not contain any characteristic bands or lines of its own.

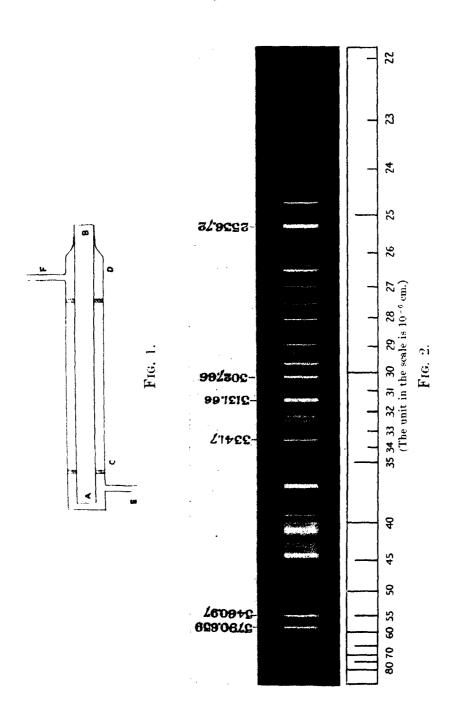
With potassium iodide a fluorescence spectrum was obtained which did not contain any of the bands of the iodine vapour fluorescence spectrum. It consisted, however, of two sets of unequally spaced fine lines, the one set lying in that portion of the spectrum between λ 4047 and λ 3840, and the other in the portion between λ 3075 and λ 2940.

V. Resonance Spectra of Iodine Vapour.

An attempt was made with the tube shown in fig. 1 to see if iodine vapour could be stimulated to the emission of resonance spectra other than those produced by the light from the mercury arc of wave-lengths λ 5790.66, λ 57696 and λ 546074. The space between the two tubes was filled with glycerine to prevent the ultra-violet fluorescence of the iodine vapour, and the tube was placed alongside of and close to a long quartz Cooper-Hewitt mercury are lamp in action. Although a number of photographs were taken with the quartz spectrograph of the light issuing from the end of the iodine tube, none of them contained lines other than those of the mercury spectrum and the lines of the resonance spectra excited by the light of the three mercury lines mentioned above. None of the lines of the mercury spectrum below λ 5460.74 and down to \$\lambda 2340 gave any indication of possessing the capacity in any degree of exciting the iodine vapour to the emission of a resonance spectrum. From this result it is evident that resonance spectra of any considerable intensity can be obtained from iodine vapour only when the latter is subjected to a stimulation by light confined to a narrow portion of the spectrum in the neighbourhood of the yellow and green lines of mercury.

VI. Summary of Results.

(1) It has been shown that fodine vapour can be stimulated to the emission of a fluorescence spectrum excited by ultra-violet light at temperatures ranging from room temperature to at least as high as 1000° C.



- (2) Iodine vapour ceases to be capable of emitting the resonance spectra discovered by Wood at some temperature below 326° C.
- (3) The wave-lengths of the light which can stimulate the ultra-violet fluorescence of iodine vapour lie between λ 2100 and a lower limit probably about λ 1800.
- (4) Resonance spectra cannot be obtained with iodine vapour when illuminated with light from the mercury arc of wave-length shorter than that of λ 5460.74.
- (5) Portions of the ultra-violet fluorescence spectrum of iodine vapour were obtained with iodoform and mercuric iodide at a temperature of about 326° C.
- (6) Mercuric iodide and potassium iodide at a temperature of about 326° C. were shown to exhibit characteristic fluorescence spectra of their own when excited by light from the mercury arc.

In conclusion the writer desires to acknowledge assistance received from Mr. P. Blackman and Mr. F. Mezen throughout the investigation.

EXPLANATION OF PHOTOGRAPH.

(PLATE 1, FIG. 2.)

The reproduction shows, in addition to the lines of the mercury arc, the bands of the ultra-violet fluorescence spectrum of iodine vapour and the lines of Wood's resonance spectra. It was taken by exposing iodine vapour in a highly exhausted tube of fused quartz to the light emitted by a fused quartz Cooper-Hewitt mercury arc lamp. The lines of the resonance spectra lie beyond $\lambda 5790^{\circ}659$. The fluorescence bands are well marked between $\lambda 3341^{\circ}7$ and $\lambda 3131^{\circ}66$, and can also be seen in the background both above and below these two limits.

The Production of Neon and Helium by the Electrical Discharge.

By J. NORMAN COLLIE, F.R.S., HUBERT S. PATTERSON, and IRVINE MASSON.

(Received July 23, 1914.)

Last year two papers were published by two of the authors (J. N. C. and H. S. P.) "On the Presence of Neon in Hydrogen after the Passage of the Electric Discharge through the latter at Low Pressures"; also a note by the third author (I. M.).† Since that time a very large number of experiments have been made, but the problem of where the neon comes from, and also the helium which was often noticed to be present, as yet has not been finally solved.

Last December a paper was read at the Royal Society by the Hon. R. J. Strutt, in which he described a new form of apparatus, and his unsuccessful attempts to obtain either neon or helium. The important point about the apparatus used was that all the operations were carried out so as to avoid transference of gases. These precautions were, as far as possible, to guard against atmospheric contamination of the gases under observation.

Of course, the authors, from the very beginning of the work, were keenly alive to the fact that the slightest leak in the apparatus meant neon and helium in the end-product. Obviously, therefore, they took every precaution to prevent it; and, as a result of the numerous control experiments to be described later, they believe that the precautions were successful.

Hitherto no description of the apparatus used has been published, and to do so in detail would be quite out of the question, for the form of the apparatus has been perpetually changed as circumstances suggested, each of the authors making his own, and more or less working along his own lines. It is necessary, however, to give as short an account as possible of the more important kinds used.

Experimental.

The coils used would each give a 12-inch spark; an ordinary hammer interrupter was used on one of them (J. N. C.), and mercury interrupters for the others. There seems to be little doubt that the nature of the break has some influence on the result of the experiment, and also that in the case of the mercury break better results have been obtained when a rectifier has been used, to produce a unidirectional discharge. Moreover,

^{* &#}x27;Chem. Soc. Trans.,' vol. 103, p. 419 (1913); 'Chem. Soc. Proc.,' vol. 29, p. 271 (1913).

^{† &#}x27;Chem. Soc. Proc.,' 1913, p. 233.

it is certainly a fact that, with the platinum break, up to July, 1913, much larger yields of neon and of helium were obtained than after this date, when new contacts were fitted. The currents used in the secondary circuit naturally varied considerably, but averaged a few milliampères.

Forms of Discharge Tube.—These ranged from simple Plücker spectrum tubes and bulbs with disc electrodes to the more elaborate jacketed forms shown in figs. 1 to 4, as well as many others not represented.

Testing Apparatus.—Several types have been used. They may be classified as "transference" and "non-transference" types, according to whether the gas under examination was introduced from outside by means of an inverted siphon over mercury after having been pumped out of the experimental tube, or whether it was admitted to the testing apparatus directly, by simply opening a tap between this and the experimental tube.

If hydrogen is present in the gas, this has to be got rid of before examination, in order that its spectrum shall not mask those of other gases which may be present. At first this was done by exploding the gas with excess of oxygen, either in an explosion burette or in the small tube used for collecting it, which had platinum wires sealed through it; the residual gas was then transferred to the Ramsay apparatus, in which oxygen and moisture are removed by cooled charcoal, and the residual helium and neon are examined spectroscopically by forcing them over mercury into a fine capillary tube with a fine platinum wire sealed through the top.

One of the present types of "non-transference" apparatus is shown in fig. 5 (H. S. P.). A is the discharge tube, whence the gases can be admitted to the dead space, in which they can be driven up to the platinum wires F to be exploded under nearly atmospheric pressure with oxygen which has been admitted from a sealed-on tube (not shown). The resulting moisture is condensed by cooling the limb C in liquid air, and the excess of oxygen is taken up by sodium-potassium alloy in the bulb D. The residual gas is examined spectroscopically in the capillary tube B.

In the other forms now used, hydrogen is removed by copper oxide heated in a hard glass tube containing also phosphorus pentoxide, and numerous other modifications have been employed.

The capillary tubes used are of the finest bore, so fine that when the mercury is once admitted it can be drawn out again only by strongly heating the tube. Rough measurements of the volume of residual gases can be made by calibrating the capillary.

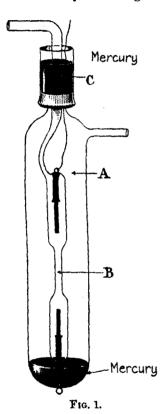
It is found that the minimum quantity of neon detectable probably equals that contained in a few cubic millimetres of atmospheric air. If, owing to defective working, the neon actually was atmospheric, the accompanying

argon could be very easily seen (as the ratio Ar: Ne in air is about 700:1), when the particular method used was such as might have eliminated nitrogen beforehand; in the apparatus depicted, nitrogen naturally made its presence at once evident if a very small part of a cubic millimetre of air was present.

Summary of Results.

In the first place, we wish to point out that a great many of our experiments have yielded negative results, for as yet unexplained reasons. In the

following we give an account chiefly of the positive experiments.



A. Different Electrodes-

Aluminium.—The apparatus used in the experiment where much helium and neon were found (J. N. C.) in the outer tube which surrounded the experimental tube* is given in fig. 1. B is the discharge tube, with moderately thick electrodes; A is the outer tube. Where the outlet tube of B passes through the neck of A, at C, was a thick piece of indiarubber tubing tightly wired and surrounded by a cup of mercury. Several modifications of this kind of tube were made later, but although small quantities of helium and neon were noticed in the outer tube, never again was the yield at all comparable with that obtained in the first experiment.

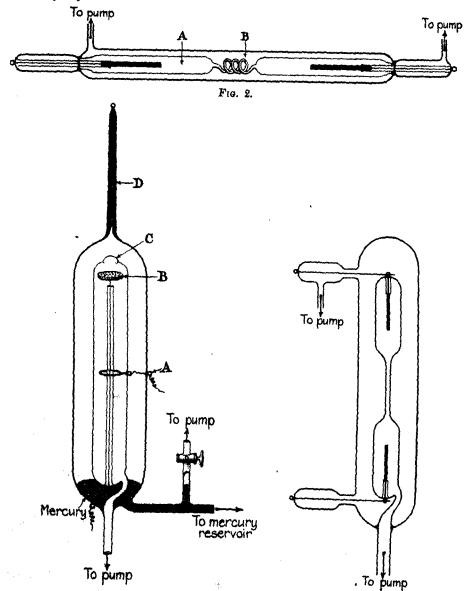
Fig. 2.—The description of an experiment with this apparatus (J. N. C. and H. S. P.) has been given.† It was designed in order that the wires connected to the electrodes in the inner tube A passed through the outer tube B

so that there were no live wires in the outer vessel. Helium and neon were found in the gases pumped off from the outer vessel. But the remarkable fact was noticed that the hydrogen (46 c.c.) admitted to the inner tube and sparked at the end of the experiment had diminished to about 0.4 c.c. Moreover, after breaking up the tube and melting the electrodes and the powdered ends of the inner tube in a hard glass tube, only 0.6 c.c. of

^{* &#}x27;Chem. Soc. Trans.,' vol. 103, p. 422.

^{† &#}x27;Chem. Soc. Proc.,' vol. 29, p. 217.

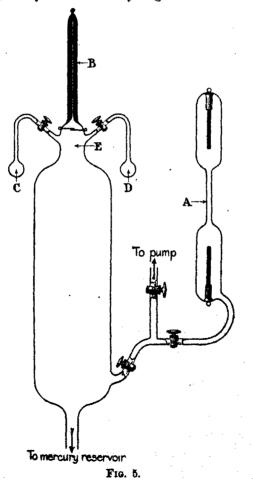
hydrogen was obtained. This apparent disappearance of hydrogen is always a noticeable fact during the discharge, and up to the present has not been entirely explained.



*The absorption of gases in vacuum tubes has been noticed by several people:—S. E. Hill ('Phys. Soc. Lond. Proc.,' Dec., 1912, p. 35) finds that hydrogen is absorbed in electrodeless tubes; Willows ('Phil. Mag.,' April, 1901), Campbell Swinton ('Roy. Soc. Proc.,' A, vol. 79 (1907)).

34 Messrs. Collie, Patterson, and Masson. Production of

A series of experiments (I. M.) were conducted with the tube shown in fig. 3. A is the anode, B a perforated cathode, C the end of the inner tube blown out thin, D a capillary tube for examining spectroscopically any gas in the outer tube by raising the mercury so as to fill the outer tube up to the bottom of D. Before beginning the trials, both inner and outer tubes were completely exhausted, after "washing" with pure oxygen, with the aid of cooled charcoal. The result of 12 experiments can be briefly summarised. Only in one experiment, viz., the second, was neon found in the gas from the outer tube, where its amount corresponded with that in about ½ c.c. of air; but it was not accompanied by any nitrogen. As to the gases in the inner tube, the first six tests were carried out with hydrogen in it, and in none of them was either neon or helium found. In the next three tests oxygen was used, and yielded similarly negative results. On again using



hydrogen (the same preparation as before), three experiments each yielded considerable amounts of neon. The quantities corresponded with that in about 1/10 to 1/5 c.c. of air; but in no case was nitrogen found in the gas. It may be remarked that in these three positive experiments, the top of the glass tube protecting the cathode rod was attacked by the discharge.

Another experiment (H. S. P.) with aluminium electrodes was carried out, using the testing apparatus of fig. 5:—

- (1) Control.—Hydrogen left in apparatus without discharge; then tested.

 No Ne nor He.
- (2) Discharge passed for 8 hours through hydrogen; tested as before.

 Ne found.
- (3) Control.—Procedure exactly as in (1). No Ne nor He.

These were repeated, with an identical result.

The chief results with other electrode materials may be tabulated. In all cases hydrogen was the gas used.

Electrodes.	Tube.	Expts.	Gases found.	Notes.	Observer.
Pd	A B B	1 1 2-8		No N ₂ . Ar test not applied. No N ₂ . Ar test not applied.	I. M. I. M.
Cu	A A A B	1 and 2 8 4 1	None	englane Market	J. N. C. J. N. C. J. N. C. H. S. P.
Pb	A B	1-8 1-4 1-5 1-5 1 1-4 1-4	He, trace Ne Good He, trace Ne Same Chiefly Ne, some He Good He, trace Ne	No decrease in 4 days, when electrodes all volatilised	H. S. P. H. S. P.

Table I.

B. Bombardment Experiments-

Tubes have been set up in which various substances could be made the anticathode. The electrodes were of aluminium. The results are given in Table II on p. 36.

It will be seen that the results are in general agreement with those obtained by Sir J. J. Thomson by the use of the positive ray method; * the chief difference which is noticed is that in our experiments nearly all of

^{* &#}x27;Rays of Positive Electricity' (Longmans Green, 1913).

Anticathode.	Experiments.	Gases found.	Notes.	Observer
Pt	1-5	He, some Ne	No decrease in yield.	H. S. P.
Ti	1-10	Good He	Non-transference. No decrease in 100 hours' use.	H. S. P.
Ur	A 1	Good He, trace Ne	Non-transference.	J. N. C.
	A 2	Pure He	Non-transference.	J. N. C.
j	B 1	Good He, trace Ne		J. N. C
\$	B 2	Pure He		J. N. C
KF	1-5	Good He		H. S. P
KCl	-	Good He	No decrease in yield.	H. S. P
KI		Fair He, trace Ne		H. S. I
RbCl	1	Strong He, some Ne		H. S. F
1,,	2	Slightly less of both		H. S. P
	8-7	Constant yield, as in 2		H. S. F
Cs.CO.	1-4	Chiefly He, some Ne		H. S. P
Ca ₂ CO ₃		Doubtful traces	Long - continued bom- bardment.	
ВеО		Same	Long continued bom- bardment.	

Table II.

the above substances gave yields of gas which did not seem to decrease even after long bombardment.

C. Mercury Arc-

The next experiments to be described arose from the observation that gas which was pumped out of an old silica mercury are lamp contained a large quantity of both helium and neon. This lamp (for which we are indebted to Mr. C. Bastian) had a tantalum anode. It was in good order when we opened it after it had run for about 4000 or 5000 hours.

A discharge apparatus was then set up. It consisted of silica throughout. Essentially, it was a n-shaped mercury are lamp with barometer-leg leads which dipped into mercury reservoirs, whereby the current entered. A side tube on one of the limbs was connected to a pump by means of a mercury-jacketed ground joint. This is a perfectly reliable method of uniting silica to glass if good rubber grease is used as a lubricant. After pumping out and washing out the apparatus with pure oxygen, the arc was started by raising the mercury reservoirs. The current taken was $\frac{3}{2}$ ampères, from a 110-volt circuit.

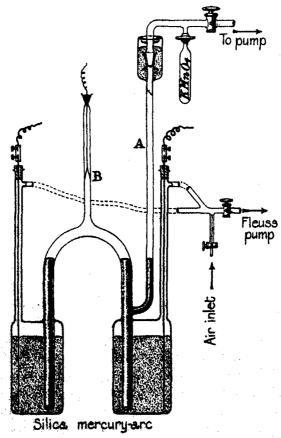
Table III shows the results of the tests, which all yielded helium. A second series was then carried out, in which the arc was jacketed with cold water, with the object of testing the possibility that atmospheric helium had diffused through the hot silica. The current taken was 5 ampères. As the table shows, the production of helium remained unaffected.

^{*} Ur powdered and heated to redness is vacuo beforehand.

Table III.—Mercury Arc (J. N. C. and I. M.).

	Hours' run.	Gas found.	Approx. quantity.
Printing one or open make you all you the street range continues one. Asset A	To a title of the second secon	Antique affects and the registering property and the services in the services and the services and a service and a	cu. mm. at 1 atm.
(12	Chiefly He; some Ne	0 001
	12	Chiefly He; less Ne	0.001
Arc unjacketed	20	Same	0 -0005
	16	Same	0.0015
į.	80	Nearly pure He	0 .001
^	5	Same	0.0002
. 1	8	Same	Very small
	20	He, trace Ne	0.0005
Are jacketed		,225, 52050 0.0	Fresh mercury
}	8	Same	0.0015
1	82	Same	0.001

This series would seem to show that the source of the helium is not diffusion from air; to throw more light on the matter, however, another silica apparatus was devised and used (I. M.). This is seen in fig. 6. It is



F1G. 6.

a n-shaped arc lamp as before, but the legs of the n are sealed into mercury reservoirs, each of which, besides bearing the wire for leading in the current, has also a connection with a Fleuss pump and an air inlet. By appropriately adjusting the pressure in the reservoirs the mercury can be set at any level in the bend. The apparatus can be exhausted by a Töpler pump connected to the tube A, which also carries a permanganate tube for generating oxygen to wash out the apparatus. The whole arrangement stands in a jar of water. During an experiment and the subsequent examination of the gas all possible communication with the outside is prevented by the mercury which cuts off from its surroundings the bend where the arc is in action. for testing the gas produced, it is simply necessary to admit air to the reservoirs so that the mercury rises into the tube B at the apex of the bend; the top half of this is very fine capillary tubing, at the top of which an extremely thin molybdenum wire is sealed through the silica to serve as one electrode in the spectroscopic examination of the gas which is thus forced into the capillary over the mercury. This apparatus thus is free from all possible objection on the score of leakage through taps or in transference and it has the advantage that a test may be made in a few minutes at any stage of an experiment.

The current used was the same as for the former apparatus. From the first, however, the arc was protected from the air by being water-jacketed, and even on continued discharge no helium or neon whatever was produced. An experiment was made in which hydrogen was admitted without affecting this result; it was noticed, however, that after about 10 minutes of passing the arc discharge the whole of the hydrogen (about 1 c.c.) had completely vanished, and the mercury could be driven practically to the top of the capillary.

The water-jacket was now removed, and a short "run" sufficed to produce a fair yield of helium. Another and longer run gave further helium and a trace of neon.

On again surrounding the arc with water, after pumping off these gases, a long run caused the appearance of a very slight trace of helium.

The results of this series point to the likelihood that the helium and neon in the silica mercury arc are atmospheric, in which case their appearance in the jacketed trials of the first apparatus would be attributed to their liberation from the walls through which they had been diffusing.

The diffusion of these gases through silica at higher temperatures is well known, but that it should occur here, where the surface temperature of the silica is only about 400°, could not have been predicted, and further experiments are in progress, as the matter cannot be regarded as being finally settled

It was stated in the second of the earlier papers that the passage of the electrodeless discharge through hydrogen had yielded helium. This was undoubtedly the case in at least one set of experiments, where large yields were obtained (H. S. P.). In repeating the experiments with slight modifications (H. S. P.; I. M.), negative results have been obtained, which seem to be related to the presence or absence of mercury vapour. Further work (H. S. P.) has partially confirmed the early results, but the conditions favourable to the production of helium are still uncertain.

Some remarks in the same paper dealt with a gas which showed a carbon spectrum, and which rapidly contracted when sparked in the examination capillary. This has been found to be merely a trace of oxygen (containing carbonaceous gas from the walls of the tube), which had remained uncondensed by charcoal cooled in liquid air, and which, when sparked with the mercury, was absorbed, forming solid oxide or ozonide of mercury.

Precuutions.

It has already been mentioned that the presence in the apparatus of the slightest amount of air, even a few cubic millimetres, would mean that neon would be found in the residual gases. The most likely way in which air might leak into the apparatus was up the fall tubes of the mercury pump and of the testing apparatus. Small bubbles of air can creep up from the rubber tube between mercury and glass, but these can be arrested by using an efficient air trap at the bottom of the fall tube. For some time we have used not one, but two such traps. Another point is, that never since the beginning of these experiments have any of the pumps, apparatus, or electrode materials been used for neon or helium. Further, in order that no traces of air should remain before commencing an experiment, pure oxygen was always admitted to the completely exhausted apparatus, and then pumped out again, the discharge tube being at the same time strongly heated with a flame. Charcoal bulbs were always heated in boiling sulphur vapour before and after each test, and the fine platinum wire at the top of the capillary spectrum tube, as well as the capillary itself, were heated and sparked to drive out any occluded gases. By these precautions all residual gas is entirely removed, and this was proved, not once, but generally between each test of gases.

If gas had to be transferred from one place to another, the small test-tubes used were cleaned by being filled once or more with pure oxygen, which was then withdrawn into a gas burette, and these tubes, containing gas over mercury, were lifted about in a small glass spoon or a porcelain crucible. By the use of proper care it is most unlikely that atmospheric contamination

could occur, and this was continually being proved by direct tests, since gases so manipulated were found to be completely free of neon or helium when subjected to testing in the usual way. Moreover, in many of the experiments, the total volume of gas used was so small that even if it had been all atmospheric air, it could not have accounted for the quantities of the neon, and still less for those of the helium, which were obtained.

The controls just mentioned also attest the purity of the gases used. The oxygen was made usually from potassium permanganate, but also by electrolysis of barium hydroxide or sodium hydroxide solution in sealed vessels, which also provided the hydrogen for many of the experiments. Hydrogen was also prepared from sodium amalgam and boiled water, from aluminium and sodium hydroxide solution (in vacuo), by heating cut sodium (in vacuo), or from palladium. From whatever source they came, the gases were not used until they were found to be pure when tested in large quantity.

Finally, the mercury has always been purified by shaking it with mercurous nitrate solution, or, more usually, by sending it in a fine spray through a long column of dilute nitric acid. The fact that no neon or helium is contained in mercury so treated was proved by several experiments (J. N. C.), in which 1000 to 1500 grm. of mercury were boiled in vacuo. On examination in the usual way, no residual gases were found whatever.

Control Tests of the Sparked Gases.—The foregoing precautions and checks afford very strong security for the successful avoidance of an air-leak in any experiment; but more direct tests were considered necessary. The most obvious one, which was exclusively relied upon in our earlier work, was the search for nitrogen. In air the ratio N₂: Ne is about 80,000:1; hence if the neon detected in an experiment came from air, the nitrogen accompanying it would be found in relatively overwhelming quantity. Trials in which very minute amounts of air were deliberately admitted and tested in the usual way verified this.

It is necessary, however, to consider whether in all possible cases atmospheric nitrogen would necessarily remain in the gas after it had leaked in. Special trials were made (I. M.) in which air at low pressure was sparked in an ordinary Plücker spectrum tube connected with the pump. Even the minutest amounts of air gave a brilliant nitrogen spectrum in this comparatively coarse method of testing: hence it is apparent that in all the experiments which we have described, in which the discharge tubes were constantly kept under spectroscopic observation and never showed the nitrogen spectrum, air did not leak in before or during the discharge. But it was found that after continued sparking of air in the Plücker tube, a green phosphorescent vacuum resulted; so that if in an experiment 1/20 c.c. of air

were to have leaked in unnoticed, after sparking for about 10 minutes there would have been no visible nitrogen spectrum. However, it was found that when the residual gas in the Plücker tube was transferred to an ordinary testing apparatus, nitrogen was plainly visible; hence, though this gas might possibly escape notice during a "run," it could be discovered in the final testing. It might be urged that even during this testing, in which the gas is spectroscopically examined over mercury, nitrogen might be absorbed so as to escape notice. Mercury was found to absorb only small quantities of nitrogen when sparked for some time with it at a low pressure, leaving a strong residual argon spectrum. A nitride of mercury was formed, which dissociated suddenly when moderately heated, and which reacted with Nessler's solution when wetted.

These considerations show that if atmospheric contamination occur at any point in an experiment after the "run," nitrogen must infallibly be detected during the examination. If any contamination occur before the "run," it would likewise instantly be made manifest on the first passage of the discharge through the experimental tube. It is only when an infinitesimally slow leak goes on during the "run" that it is possible that no nitrogen could be seen at any time; and to provide against this contingency an additional control is necessary, namely the absence of argon from the gas. It was proved that this is a reliable test by the trials made in the Plücker tube before mentioned. Though no argon spectrum could, with certainty, be seen in the Plücker tube after continued discharge, the residual gas when put into the testing apparatus gave a strong argon spectrum.

Besides this, it was found that if atmospheric gases have been bombarded into the aluminium electrodes of the Plücker tube, the neon can be extracted again (by heating and by passing the discharge) in a comparatively short time, together with much larger quantities of the argon. The whole of the absorbed argon is not, however, so readily extractable, and it appears that this gas is held with much greater tenacity than is neon when it has once been bombarded into the electrodes. This signifies that the argon test is in reality superfluously delicate as a control; nevertheless, it was used.

In all experiments where helium was the chief product, atmospheric contamination is ipso facto excluded; and as far as our tests have yet been carried, contamination seems to be thoroughly excluded in all the experiments. It must be mentioned, however, that in the less recent stages of the work, the disappearance of nitrogen during discharge was not properly understood; hence it is quite possible that some of the experiments in which the nitrogen test was exclusively relied upon may have been vitiated by a very minute and systematic leakage during discharge.

Possible Sources of the Gases.

Before coming to this question, we may make some tentative suggestions as to why Strutt's work proved unsuccessful; but at the same time it should be pointed out that many of our own experiments have been equally unsuccessful.

- (1) A large charcoal bulb undoubtedly absorbs neon. A charcoal bulb of the same size as was used by Strutt in his testing apparatus, and a small one such as we always used, both with taps, were sealed on to a "nontransference "apparatus (J. N. C.). One cubic centimetre of air was taken, and the small bulb was cooled in liquid air. The residual neon occupied 26 scale-divisions of the capillary at about 1-2 mm. pressure. The gases were then boiled out of the small bulb and the large one was cooled instead for one hour. Residual neon = 8 divisions at as nearly as possible the This residue was washed out with oxygen and rejected, same pressure. meanwhile keeping the tap of the large bulb closed. The tap was now opened, the large bulb warmed up, and the gases from it exposed to the small bulb, which was once more cooled in liquid air. The residual gas was neon, and it occupied 15 divisions. Hence the large bulb had absorbed two-thirds of the relatively very large quantity of neon introduced. The experiment was repeated in several ways, always with the same result; and when only a very little neon was put into the apparatus, it was found that the large bulb absorbed it all, if small successive quantities of oxygen were admitted to the dead space so as to wash residual neon into the charcoal.*
- (2) The capillary used by Strutt was closed with wax and had an outside electrode. We have always found it necessary to use a fairly strong discharge through the platinum wire which closes the top of the capillary; and further to be sufficiently sensitive the capillary tubes must be so fine that mercury can only be driven down out of them by strong heating.
- (3) Any "splashed" metal in the experimental tube pertinaciously retains neon and helium unless it is strongly heated during withdrawal of the gas.
- (4) The nature of the discharge through the experimental tube has, as was mentioned, a considerable influence upon the yield, and the necessity for a unidirectional current has already been pointed out.

Whatever the causes may be, it may be remarked that Strutt's results are in opposition not only to many of our own, but also to those of Sir J. J.

^{*} It is necessary to qualify this criticism by mentioning that, despite the use of large charcoal bulbs, Strutt was able to detect the neon in 0.01 c.c. of air.

Thomson, which appear substantially to corroborate ours by an independent method.

A paper has recently been published by Mr. G. Winchester.* By using a very high potential discharge in tubes with a high vacuum he finds that the gases hydrogen, helium, and neon are set free. He also notices the uncertainty of production during experiment: in his paper he says:-" One thing noticeable in tubes of this kind is that, whereas some yield only comparatively small amounts of helium, others are very rich in this gas. One tube which at first gave only a small amount of helium in comparison · with hydrogen, suddenly after running for 15 days gave out an enormous amount of helium for a few days and then suddenly became normal again. Since then I have found two tubes that showed the same phenomenon. Some electrodes seem to be very rich in helium and some very poor. All the aluminium electrodes mentioned in this paper were made of c.p. aluminium unless otherwise stated." Mr. Winchester believes that the helium and neon have been absorbed by the electrodes from the air, but that the case of hydrogen is different, and that there is a possibility of its being a disintegration product of the metal.

There remains the question: Since the neon and helium do not seem to come from leakage of air, what other origin is possible? Two hypotheses which suggest themselves are: Permeation from the air through the walls of the discharge tubes, and previous occlusion in the materials of the discharge tubes.

- (1) Permeation.—It was conceivable that under the influence of heat and the discharge, glass might be permeable to helium and also to neon in much the same way as hot silica. It was proved that heat alone was unable to accomplish this, and experiments already described, in which the discharge tubes were enclosed in atmospheres of helium and of neon with negative results, disprove this hypothesis. In any case the vacuum jackets with which most of the tubes were provided would have prevented any permeation. Nor do the platinum wires sealed through jacket and discharge tube act as avenues for the entry of these gases, as is shown by the positive results obtained with the gases sparked in tubes like that shown in fig. 4, where the outer sealed wire merely touches the inner one and is not continuous with it. These facts render the occasional appearance of helium and of neon in the outer jackets all the more unaccountable.
- (2) Occlusion.—Especially in view of the fact that in some experiments the yield of neon appeared to cease after some time of running, the hypothesis

^{* &#}x27;Physical Review,' N.S., vol. 3, No. 4, April, 1914.

⁺ J. N. C., los. oit., I, p. 422.

44 Messrs. Collie, Patterson, and Masson. Production of

that the materials of the tubes already contained these gases is an obvious one. It has been experimentally put to the test, and so far appears to be untenable.

In the first place, the positive results with the electrodeless bulb and those with the mercury arc seem to be strong evidence against the metals used being the source—in the latter case, since boiling the mercury in vacuo yielded neither gas, as has been explained. This has been further studied, however, by examining aluminium. It has been melted in vacuo and the evolved gases tested (J. N. C.; I. M.). They contained no neon nor helium. To make perfectly certain, however, a fresh piece, about \(\frac{1}{4} \) inch long, of the same wire as was used for electrodes in successful experiments, was allowed completely to dissolve in potassium hydroxide solution in an apparatus whence all traces of air had first been removed. The hydrogen was passed directly over hot copper oxide, thence the residual gases could be washed directly into the large dead-space of a "non-transference" apparatus with the help of a little oxygen from a sealed-on permanganate tube. There was neither neon nor helium in the gas (I. M.). This experiment has been made in other ways with the same result.

Since the metals contain neither of these gases, the only other possible store of pre-existing neon and helium would be the glass walls of the tubes. This has been tested as follows:—

Melting the glass in vacuo yielded neither neon nor helium. A large quantity of the same glass as was used for making the tubes was powdered and was acted on by potassium fluoride and strong sulphuric acid in an apparatus so arranged that no trace of air was present, the only gas being a little pure oxygen. Between 300 and 400 c.c. of silicon fluoride were collected and were frozen out by liquid air. The residual gases contained no neon and no helium (J. N. C.). To see if older glass contained the gases, two specimens were melted in a hard glass tube in vacuo and the gases tested. One was a green glass (Roman), probably from Egypt and presumably at least 1500 years old; the other was an opaque yellow glass (Chinese, Kienlung period), about 150 years old. Neither specimen yielded neon or helium.

Valuable support is lent to these experiments, which negative the occlusion hypothesis, by tests described by Sir J. J. Thomson,* who found that aluminium salts gave the same quantity of helium on bombardment by cathode rays, whether they were made from ordinary aluminium metal or from the same metal which had originally had helium actually forced into it by being made the electrode of a helium spectrum tube. This shows, as he says

that "solution can be relied upon to eliminate adsorbed gas." Again, the same author describes how lead which is boiled in vacuo gives off no helium, but does so when bombarded; this appears to us to mean that no helium pre-exists in the lead.

It would be unreasonable in the extreme to suppose that, if helium and neon were present as such in any of the materials used, they would not be set free on dissolution which is accompanied by gas evolution. Solution of aluminium, for example, in potassium hydroxide entails a far more thorough physical disintegration of the piece of metal than does bombardment of its surface. The only tenable supposition is that any inert gases physically admixed must be set free; and we are not justified in assuming anything but a physical admixture in the case of inert gases pre-existing in aluminium or in glass. The proved absence of neon and of helium from the resulting products of chemical action must, therefore, mean that they are absent altogether.

We have endeavoured to put the facts of the case as fully as possible, without reference to any preconceived theory. It is not our view that our experiments rigidly exclude all the possibilities which have been mentioned; but it is evident that the trend of the results is towards conclusions which, if they turn out to be true, would be of very obvious importance.

We wish to thank Dr. H. T. Clarke for his assistance during part of the work.

* 'Nature,' vol. 90, p. 646 (1913).

On the Flow of Viscous Fluids through Smooth Circular Pipes.
By Charles H. Lees, D.Sc., F.R.S.

(Received October 1, 1914.)

1. The problem of the flow of a viscous fluid through a tube of circular section is of considerable interest both to physicists and to engineers. Since Stokes* showed the connection between the viscosity of the fluid and the empirical formula given by Poiseuille† for the rate of slow or stream-line flow of the fluid through a capillary tube, the tube method has been one of the most useful and accurate for the determination of viscosity.

On the other hand, the extensive use of pipes for the transmission of gas, compressed air, water and oil, at speeds much above those which obtain in a Poiseuille experiment, rendered it necessary to investigate the laws of "turbulent" flow of viscous fluids through tubes, and there are at the present time several formulæ in use by engineers giving the mean rate of flow of such a fluid through a pipe in terms of the dimensions of the pipe and the difference of pressure between its two ends.

Of the purely empirical formulæ at first used, that of Hagen, according to which the difference of pressure p_0-p_l between two sections l apart of a pipe of diameter d was given by $p_0-p_l=flv^{1.75}/d^{1.26}$, where f is a constant and v the mean velocity, deserves mention owing to its approximation to the truth for incompressible liquids as shown by later work.

Weisbach modified the older equation $p_0 - p_l = f l v^2 / d$ by introducing instead of v^2 , $v^2 + (7/6)v^{1.5}$, and this proposal, as will be seen in the sequel, is on the right lines, and gives a fair approximation to the facts so far as they relate to the effect of change of speed.

- 2. Reynolds placed the power formulæ on a rational basis by showing that if the fall of pressure per unit length of the pipe depended on powers of the density ρ , viscosity η , and mean speed v of the fluid, and on the diameter d of the pipe, it must be expressible as $f(\eta/\rho)^{2-n}v^n/d^{3-n}$, where f and n are constants. From the observations of Darcy he deduced values of n varying
- * Stokes, 'Camb. Phil. Trans.,' vol. 8, p. 304 (1847). If p_0 , p_l are the pressures at the two ends of a horizontal capillary tube of diameter d and length l, through which a fluid of viscosity η flows with mean velocity v, then $p_0 p_l = 32 l \eta v / d^2$.
 - † Poiseuille, 'Comptes Rendus,' vol. 15, p. 1167 (1842).
 - ‡ Hagen, 'Math. Abh.,' Berlin Akad. (1854), p. 17.
 - § Weisbach, "Mechanics," quoted in Gibson, 'Hydraulics,' p. 197.
 - || Reynolds, 'Phil. Trans.,' vol. 174, p. 935 (1883); 'Scientific Papers,' vol. 2, p. 97.
- T Darcy, 'Comptes Rendus,' vol. 38, pp. 407 and 1109 (1854), and 'Mémoires Acad. des Sciences,' vol. 15, p. 141 (1858).

from 1.79 for glass and lead pipes to 1.88 for new and 2.0 for old cast iron pipes.

This not proving sufficiently general to cover all the observations available, Unwin* proposed the modified expression fv^n/d^x , and found values of n from 1.72 for wrought iron and tin plate to 1.95 for new and 2.0 for old east iron pipes, while x varied from 1.1 for tin plate to 1.16 for new and old cast iron and 1.39 for wrought iron.

3. The important results which have been obtained by Dr. Stanton† and by Dr. Stanton and Mr. Pannell‡ at the National Physical Laboratory during the last three years from observations of the flow of air, oil, and water through smooth brass pipes of diameters from 0·3 to 12 cm. at speeds from 5 to 5000 cm. per second, seem by their accuracy and consistency to justify a re-examination of the subject with a view to the establishment if possible of a connection between the physical properties and mean speed of the fluid and the diameter, length, and pressure of the pipe, which shall hold with greater accuracy and over a wider range than the existing formulæ have proved themselves capable of doing.

The data available for the examination of the flow in smooth pipes, e.g. drawn brass or lead or bitumen covered pipes, include, in addition to the results given by Stanton and Pannell, those of Saph and Schoder§ on water in pipes from 0.3 to 5 cm. diameter, which agree very closely with those of Stanton and Pannell, except near the lower limit of speed when the flow is changing from the turbulent to the stream-line type; those of Darcy|| on water in lead or bitumen covered pipes from 3 to 28 cm. diameter, which give resistance to flow rather greater than those found by the former observers but varying with speed apparently according to the same law, and those of Reynolds¶ on water in lead tubes 0.6 and 1.3 cm. diameter, which give less resistance than any of the others but apparently show the same law of variation with speed. Stanton and Pannell give a graphical comparison of all these results in fig. 5, p. 212, of their paper.

4. On the theoretical side of the investigation we have the "Principle of Dynamical Similarity," which, whether established by an examination of the

^{*} Unwin, 'Industries,' vol. 1, p. 51 (1886). Résumés of the present position of the subject will be found in Unwin's article "Hydraulics," in the 'Encyclopædia Britannica,' 11th edition, and in Gibson's 'Hydraulics.'

⁺ Stanton, 'Roy. Soc. Proc.,' A, vol. 85, p. 366 (1911).

[†] Stanton and Pannell, 'Phil. Trans.,' A, vol. 214, p. 199 (1914).

[§] Saph and Schoder, 'Amer. Soc. Civil Engs. Proc.,' vol. 51, p. 253 (1903).

Darcy, 'Mémoires Acad, des Sciences,' vol. 15, p. 141 (1858).

T Reynolds, 'Phil. Trans.,' A, vol. 174, p. 964 (1883).

equations of motion of the fluid, as by Stokes* and Helmholtz,† or by the doctrine of dimensions of physical quantities, as by Rayleigh,‡ shows that for the flow of viscous fluids through pipes, if for a number of cases vd/ν has the same value, where v is the speed, d the diameter of the pipe, and ν the kinematical viscosity, then for the same cases $R/\rho v^2$ will have the same value, where R is the resistance per unit surface of contact of fluid and pipe. Hence, if vd/ν be taken as the abscissæ, and $R/\rho v^2$ as the ordinates, every case of motion of a viscous fluid through a pipe will be represented by a point of the diagram, and the whole of the points will lie on a curve if the principle is strictly applicable to such cases, but will cover a strip of width which will increase as the applicability of the principle decreases.

The observations made by Stanton and by Stanton and Pannell on the flow of air and water through pipes show that the locus of the points in the diagram, if v, the velocity, be taken as the mean velocity over the whole section of the pipe, is a narrow strip the width of which is only of the order of the errors of experiment, and that for cases in which vd/ν is the same, the law of distribution of velocity over the cross section is the same.

Understanding by v in the above statement of the principle, the mean velocity of flow, one of the most important results of the National Physical Laboratory experiments is the proof of the applicability of the Principle of Similarity to the turbulent flow of fluid in pipes, although the eddies set up in the pipes may not have dimensions in the same ratios as the diameters of the pipes, which the principle strictly demands.

Taking then $R/\rho v^2$ to be a function of vd/ν , that is $R/\rho v^2 = \phi (vd/\nu)$, it remains to determine the simplest form of the function ϕ which will embody the results of Stanton and Pannell and of Saph and Schoder, which are in close agreement and appear to be much more accurate than the results previously available.

The curve given by the former observers connecting $R/\rho v^2$ with $\log{(vd/\nu)}$ suggests a relation of the hyperbolic type, and on plotting $\log{(R/\rho v^2)}$ as ordinates against $\log{(vd/\nu)}$ as abscisse the curve was found to be slightly concave upwards, showing that the resistance per unit surface R cannot be expressed as a single power of the mean velocity v throughout the whole range of the experiments. As the original curve given by Stanton and Pannell suggests that $R/\rho v^2$ approaches a finite limit other than zero as vl/ν increases indefinitely, curves of $\log{(R/\rho v^2-a)}$ as ordinates against

^{*} Stokes, 'Camb. Phil. Soc. Trans.,' vol. 9, Pt. 2, p. [19] (1850); 'Math. and Phys. Papers,' vol. 3, p. 17.

[†] Helmholtz, 'Berl. Ber.,' 1873, p. 501; 'Wise. Abh.,' vol. I, p. 158.

[‡] Rayleigh, 'Aeronautica Report,' 1911-1912, p. 97.

 $\log{(vl/\nu)}$ as abscisse were then plotted with various values of a, and it was found that with a = 0.0009 the curve became a straight line, the slope of which indicated that $\log_{10}{(R/\rho v^2 - a)}$ plus 0.35 times $\log_{10}{(vd/\nu)}$ was a constant = -1.116, or that

$$(R/\rho v^{2} - 0.0009) (vd/\nu)^{0.35} = 0.0765.$$
Hence
$$R/\rho v^{2} = 0.0009 + 0.0765/(vd/\nu)^{0.35},$$
or
$$R = \rho v^{2} [0.0765 (\nu/vd)^{0.35} + 0.0009],$$

$$= \rho [0.0765 (\nu/d)^{0.35} v^{1.65} + 0.0009 v^{2}].$$
(1)

Since this expression satisfies the principle of similarity which Stanton and Pannell have shown holds for the mean speed of flow of air and water through pipes of diameters between 0.3 and 12 cm., the constants of the above equation hold over the whole of this range at least, and probably this type of relation with a small change of the constants will apply over a much wider range. The viscosity of the fluid only enters into the expression through the term $(\nu)^{0.35}$, and has only a small influence on the result. Taking the temperature as 15° C, the values of ν for water and air are 0.0114 and 0.137 respectively, and the values of $(\nu)^{0.35}$, 0.25, and 0.50 respectively.

Hence for water at 15° C.

$$R = 0.0191r^{1.65}/d^{0.35} + 0.0009r^2,$$

and for air at 15° C, and 76 cm, pressure

$$R = 0.0000468 \, e^{1.65} / d^{0.35} + 0.00000110 \, v^2.$$

In many technical cases it is not R, the resistance per unit area of surface exposed to the fluid, which is required, but the fall of pressure $p_0 - p_l$ along a given length l of pipe due to it.

Taking the length l of pipe to be short enough to allow changes of density of the fluid to be neglected we have

$$R\pi d/2 = \pi d^{2}(p_{0}-p_{l})/4l,$$

$$R = d(p_{0}-p_{l})/2l,$$

and for any fluid

$$p_0 - p_l = l\rho \left(0.153 \nu^{0.35} v^{1.45} / d^{1.35} + 0.0018 \nu^2 / d\right)$$

= $\{l\rho v^2 / d\} \{0.153 (\nu / \nu d)^{0.35} + 0.0018\}.$ (2)

In the case of water at 15° C. this reduces to

$$p_0 - p_l = l (0.0382 v^{1.65}/d^{1.35} + 0.0018 v^2/d);$$

and in the case of air at 15° C. and 76 cm. pressure,

$$p_0 - p_1 = l (0.0000936 v^{1.65} / d^{1.35} + 0.00000220 v^2 / d).$$

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In order to show how nearly the formula reproduces the observations of Stanton and Pannell their original diagram is reproduced in the accompanying figure, with a line drawn on it to show the values deduced from the expression. It will be seen that the agreement is as close as could be expected.

It will be noticed from the form of the final expression for the fall of pressure along the tube, that this fall will, for all velocities, be approximately proportional to a power of the velocity between the 1.65th and the 2nd, and that as the speed or diameter increases or the kinematical viscosity decreases the law of variation will approximate more and more closely to the second power. This result was obtained by Stanton and Pannell* in the case of the flow of water through a pipe of 1.26 cm. diameter. For mean speeds of 58, 258, 900 and 2250 cm. per second the powers of the velocity were 1.72, 1.77, 1.82, and 1.92 respectively.

Gibson† found the same result for the flow of brine of various strengths through smooth brass pipes of diameters from 0.75 to 1.5 inch. Thus for the smallest pipe for speeds between 2 and 10 feet per second the resistance was found to vary as the 1.785th power of the mean velocity and for the largest pipe and the same speeds as the 1.795th power.

He was unable to detect any influence of the kinematical viscosity on the value of the index from water to the strongest brine he used, for which the density was 1:134 and the kinematical viscosity 1:28 times that of water.

In order to arrive at some quantitative estimate of the agreement of these results and the formula given, it is necessary, since most observers have embodied their results in single power of the velocity formulæ, to find in each case the best single power formula which will represent the complete formula over the limited range of any particular set of experiments.

The accuracy of the representation will be sufficient for the present purpose if the single power expression cv^n has its constants c and n so determined that its value and the value of its differential coefficient with respect to v are identical, for a particular value of v given by the experiments, with the value given by the complete expression for the same value of v.

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That is cv^n = l\rho \left[ 0.153 \left( v/d \right)^{0.35} v^{1.65} + 0.0018 \, v^2 \right], and cnv^{n-1} = l\rho \left[ 0.2525 \left( v/d \right)^{0.35} v^{0.66} + 0.0036 \, v \right], or cvv^n = l\rho \left[ 0.2525 \left( v/d \right)^{0.35} v^{1.65} + 0.0036 \, v^2 \right]. Hence n = \left[ 0.2525 \left( v/vd \right)^{0.35} + 0.0036 \right] / \left[ 0.153 \left( v/vd \right)^{0.35} + 0.0018 \right] = 2 - 29.7 / \left[ 85 + \left( vd/v \right)^{0.35} \right]. * Stanton and Pannell, 'Phil, Trans.,' A, vol. 214, p. 211. † Gibson, 'Inst. Mech. Engs. Proc.,' Feb., 1914.
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Using this expression, we have for the best values of n at the points given by Stanton and Pannell the following Table:—

Tr. 1	n		
Velocity, cm/sec.	. Calculated.	Observed. (Stanton and Pannell	
58	1 .72	1 .72	
25 8	1 .76	1 .77	
900	1 '79	1 .82	
2250	1 .62	1 92	

The agreement is as good as could be expected, when we remember that the values are each calculated for a point of the resistance velocity curve, while the observed values represent means over considerable lengths of the curve.

Taking Gibson's observations on smooth pipes of diameters 1.90 and 3.81 cm., through which water or brine passed, with a mean speed of 180 cm. per second, we have the following Table:—

Mean Speed 180 cm./sec.

			•	
	Fluid.	Density.	n	
Diameter.			Calculated.	Observed by Gibson.
cm. 1 '90 8 '81 1 '90 8 '81	Water Brine	1 ·0 1 ·184	1 ·754 1 ·773 1 ·748 1 ·766	1 ·785 1 ·795 1 ·785 1 ·795

The agreement is satisfactory, and the values of the indices for water and for the strongest brine are sufficiently alike to account for the difficulty in distinguishing them experimentally.

Caruthers* found for the flow of Texas fuel oil through rough pipes of diameters from 2 to 10 feet that the resistance varied as $v^{1.6}/d^{1.2}$. This expression lies outside the range of the present formula, but Caruthers does not attach much weight to the indices he adopts.

5. So far as the effect of temperature on the difference of pressure is concerned, it is almost entirely confined in the case of liquids to the term

^{*} Caruthers, 'Roy. Soc. Proc.,' A, vol. 87, p. 154 (1912).

in ν . For water $\nu^{0.35}$ has the values 0.208, 0.179, 0.148 at 15°, 35°, and 70° C. respectively, and the values of the first term of the expression for the fall of pressure will be in the same ratios. Since the ratio of the value of this term to that of the complete expression decreases as the diameter of the tube increases and as the speed increases, the effect of temperature on the resistance of the pipe will be smaller as the diameter increases and as the speed increases. In the case of a smooth brass pipe 3.81 cm. in diameter, through which water flowed, with speeds from 120 to 1000 cm. per second, Mair* found that the mean relative resistances at 13.4°, 33.2°, and 71° C. were as 1:0.87:0.74. According to the formula given above, they should be as 1:0.86:0.70 at the lower and as 1:0.92:0.81 at the upper limit of speed. The agreement is as close as could be expected without a more detailed examination of the distribution of Mair's results about the mean he gives.

It is evident from the formula that as the resistance approximates more closely to the v^2 law as the diameter of the pipe or the velocity of the fluid through it increases, the effect of changes of temperature on the first term becomes relatively less important. Thus Mair states that when the resistance varies as the 1.8th power of the speed it decreases 0.6 per cent. per degree Centigrade and when the resistance varies as the 1.9th power of the velocity it only decreases 0.25 per cent. per degree.

It is thus evident that the proposed formula reproduces the experimental facts at present known much more closely than any previous expression has succeeded in doing. As it has been deduced from experiments on smooth pipes it is not strictly applicable to rough pipes, although measurements on such pipes give results which appear to follow the same general laws as those for smooth pipes. Before greater precision in the laws of flow through such pipes can be attained it will be necessary to come to some understanding as to the specification and measurement of the degree of roughness of a surface.

- 6. The conclusions arrived at may be summarised as follows:
- (1) The difference of pressure $p_0 p_l$ in dynes per square centimetre between two sections distant l cm. from each other along a pipe of diameter d cm. through which a fluid whose density ρ may be considered constant over the length l and whose kinematical viscosity is ν is flowing with mean velocity ν cannot be represented by a single power of the velocity but requires for its expression a formula of the type

$$p_0-p_1 = \{l\rho v^2/d\} \{a+b (\nu/vd)^n\},$$

where a, b, and n are constants.

^{*} Mair, 'Inst. Civil Engs. Proc.,' vol. 84, p. 424 (1886).

- (2) To the extent to which the Principle of Dynamical Similarity is applicable to the flow of fluid in tubes, a, b and n should be absolute constants applicable to all fluids and all tubes. Stanton and Pannell's results show that over a wide range a = 0.0018, b = 0.153 and n = 0.35.
- (3) As the velocity and diameter increase and as the kinematical viscosity decreases the pressure difference varies more nearly as $l\rho v^2/d$.
- (4) The effect of temperature on the pressure difference decreases as the velocity and diameter increase and as the kinematical viscosity decreases.

The Silver Voltameter. Part III.—The Solvent Properties of Silver Nitrate Solutions.

By T. MARTIN LOWRY, F.R.S.

(Received June 18,—Read June 25, 1914.)

In an earlier paper by Mr. F. E. Smith* and a second paper by the author in conjunction with Mr. F. E. Smith it was shown that the weight of silver deposited by a given current was influenced in a very important degree by impurities in the silver nitrate solutions. The most important impurities are those which are capable of exerting a reducing action upon the silver nitrate. But there is also a group of substances to be considered which are soluble in silver nitrate solutions, though almost insoluble in water: these are precipitated when the silver nitrate solutions are impoverished at the cathode by the passage of the current and cause an appreciable increase in the weight of the deposit. They may be removed by diluting the silver nitrate solutions, filtering off the precipitated impurities, evaporating the filtered solution and draining the crystals of silver nitrate which separate; any impurities that may have escaped precipitation will be freely soluble in the concentrated mother-liquor from which the crystals have separated, and may be got rid of in the usual way by draining on the pump and rinsing cautiously with water.

In view of the importance of these impurities in the experimental determination of the electrochemical equivalent of silver, and the interest of the

* Part I, "A Comparison of Various Forms of Silver Voltameters," by F. E. Smith, A.R.C.Sc., and "A Determination of the Electro-chemical Equivalent of Silver," by F. E. Smith, A.R.C.Sc., and T. Mather, F.R.S. ('Phil. Trans.,' A, vol. 207, pp. 545-581, (1908)); Part II, "The Chemistry of the Silver Voltameter," by F. E. Smith, A.R.C.Sc., and T. M. Lowry, D.Sc. ('Phil. Trans.,' A, vol. 207, pp. 581-599 (1908)).

problem from the standpoint of the theory of solutions, it appeared to be desirable to pursue the matter further and to make quantitative measurements of the solvent properties of silver nitrate solutions for some typical substances which are insoluble, or nearly so, in pure water. The present paper includes measurements of the solubility of silver chloride, bromide, iodide, and sulphide. The solubility of the iodide has already been investigated somewhat fully by Hellwig,* but only a few incidental measurements have been made in the case of the other salts.

A. SILVER CHLORIDE.

(With F. Hawkes, J. F. Potts, B.Sc., and R. G. Parker, B.Sc.)

In determining the conditions that were most favourable for the precipitation of silver chloride and silver bromide, Stas found† that the solubility of these compounds was diminished by the presence of an excess either of silver nitrate or of the soluble halogen salt. This is in accordance with the law of mass-action, according to which the action

$$AgNO_3 + KCl \implies AgCl + KNO_3$$

should be driven towards completion (left to right) by the presence of an excess of either of the substances shown on the left-hand side of the equation.

It has long been known, however, that the contrary effect takes place in more concentrated solutions. Thus Berthollet, in 1799,‡ discussing the problem of removing small quantities of hydrochloric from nitric acid, writes as follows:—

"Muriate of silver being much less soluble than muriate of lead, silver is therefore much better than lead for retaining the muriatic acid mixed with nitric acid; yet Welter and Bonjour have observed that some muriatic acid always passes by distillation, if the precautions indicated by those learned chemists were not attended to. To obtain nitric acid pure in a direct manner it is necessary that the acid to be distilled be diluted, so that it may not have strength sufficient to dissolve muriate of silver, and that the muriate of silver which is precipitated be separated before the fiquid be submitted to the action of heat; still better, the muriatic acid of nitrate of potash may be precipitated by a solution of silver; and by decomposing afterwards the nitrate of potash, nitric acid will be obtained quite pure, and free from muriatic acid."

Berthollet's observation is again in agreement with the law of mass-action. But precisely similar effects are produced by concentrated solutions of

^{* &#}x27;Zeitschr. Anorg. Chem.,' vol. 25, pp. 157-188 (1900).

^{† &#}x27;Œuvres,' vol. 1, pp. 87-194.

^{1 &#}x27;Chemical Affinity,' English translation, p. 178.

hydrogen chloride or of common salt (see, for instance, Barlow*), both of which might be expected, by a simple application of the law of mass-action, to produce a diminution of solubility. The solvent properties of concentrated solutions of silver nitrate are less widely known, but the effects produced are quite as important as those which are observed in the case of hydrochloric acid and common salt.

It is not the purpose of the present paper to discuss fully the origin of these remarkable solvent influences; but it may be suggested that (in accordance with the general principle that "like dissolves like") fused silver nitrate is probably an excellent solvent for silver chloride and that the behaviour of its concentrated aqueous solutions may be interpreted in much the same way as that of other mixed solvents. The case appears to resemble the use of a mixture of alcohol and water to dissolve an organic compound such as camphor, the solubility of which in dilute aqueous alcohol is very small, but increases rapidly as the concentration of the alcohol in the mixture is increased.

Solubility of Silver Chloride in Silver Nitrate (Gravimetric Method).

The solubility of silver chloride in aqueous silver nitrate was measured by two methods—

- (a) By gravimetric analysis at 20° C.
- (b) By volumetric analysis over a range of temperature, up to about 100° C.

In the gravimetric analysis a considerable quantity of silver nitrate was dissolved in less than half its weight of water, and a precipitate was formed by adding a known quantity of a standard salt solution. The mixture was stirred in a large test-tube, supported in a thermostat heated to 20° C. After a time, the precipitated silver chloride was allowed to settle, the bulk of the clear liquid was decanted and the precipitate was collected on a weighed Gooch crucible. After draining away as much as possible of the concentrated silver nitrate solution the silver chloride was washed, dried, and weighed.

The weight of the precipitate obtained in this way was much less than when the salt was precipitated from a dilute solution by a small excess of silver nitrate. A considerable proportion of silver chloride had therefore been retained by the silver nitrate, when present in great excess and in a concentrated solution.

The whole of the silver solutions, including the earlier washings from the Gooch crucible, were then collected, made up to a known weight with water, warmed to ensure complete saturation with silver chloride, and again stirred

^{* &#}x27;Amer. Chem. Soc. Journ.,' vol. 28, p. 1446 (1906).

in the thermostat at 20° C. A further quantity of silver chloride was thus thrown down, and this was collected and weighed as before. This process was repeated until almost the whole of the silver chloride had been collected.

In a preliminary series of experiments 120 grm. of silver nitrate were mixed with 19:987 grm. of a decinormal solution of sodium chloride in presence of quantities of water amounting altogether to 60 grm. in the first and 240 grm. in the final measurement. Out of a total weight of 0:2868 grm. AgCl, the quantities precipitated and retained were:—

AgNO ₈ .	Water.	AgCl precipitated.	AgCl retained.	AgCl retained per 100 grm. AgNO ₃ .
grm.	grm.	grm.	grm.	grm.
120	60	0 1220	0 1648	0 ·1390
120	90	0 ·0670	0 0978	0 ·0815
120	120	0 ·0255	0 0728	0 ·0602
120	240	0 ·0469	0 0254	0 ·0212

These measurements showed the general nature of the effects which might be expected, and indicated the conditions that were necessary for successful working. The second and final series of measurements was made with 220 grm. of silver nitrate and 30.0558 grm. of N/10 salt solution, which should have given 0.4314 grm. AgCl. The silver chloride precipitated and retained was as follows:—

Table I.—Solubility of Silver Chloride in Silver Nitrate at 20° C.

AgNO ₃ .	Water.	AgC1 precipitated.	AgCl retained.	AgCl retained per 100 grms. AgNO ₈ .
grm.	grm.	gru.	grin.	grm.
22 0 22 0	110 165	0 ·1296 0 ·0800	0 ·3018 0 ·2218	0 1872 0 1009
220	220	0.0630	0.1588	0.0722
220	830	0.0704	0.0884	0.0402
220	440	0.0238	0.0646	0.0294

It will be seen that the quantities of silver chloride retained per 100 grm. of silver nitrate in presence of 50 grm. of water agree closely in the two series of experiments, namely, 0.1390 and 0.1372 grm. The quantities retained after dilution are too small in the preliminary series, because local precipitation had taken place on dilution, and the necessity of warming the solutions to secure complete saturation had not been discovered.

The rapid diminution of solubility by dilution with water is shown in fig. 1.

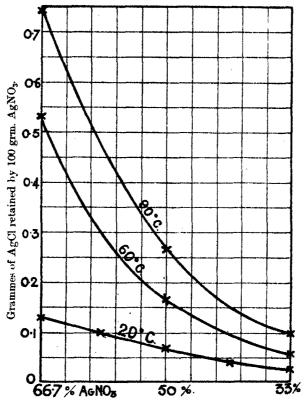


Fig. 1.—Influence of Dilution on the Solubility of Silver Chloride in Silver Nitrate Solutions.

Solubility of Silver Chloride in Silver Nitrate (Volumetric Method).

The volumetric method of measurement has the advantage of providing data for a wide range of temperatures almost up to the boiling point of the solutions; it can also be carried out with much smaller quantities (5 to 10 grm.) of silver nitrate.

The silver nitrate was weighed into a test-tube provided with a thermometer and a small stirrer passing through a rubber stopper. A known quantity of water, containing a suitable amount of salt in solution, was added under such conditions that a clear solution was obtained. The test-tube containing the hot solution was then placed in a beaker of hot water and allowed to cool slowly, with constant stirring, until it became opalescent by the separation of silver chloride. It was found that this effect could be detected far more readily when the test-tube was surrounded by clear water

for comparison than when it was cooled in air, and that stirring was essential to prevent supersaturation. The temperature of saturation could be fixed within about a degree. By varying the proportions of water, silver nitrate, and salt, complete temperature-solubility curves could be plotted for any given ratio of silver nitrate to water.

The following data were obtained:- "

Table II.—Solubility of Silver Chloride in Silver Nitrate at Different Temperatures.

$AgNO_8$.	NaCl N/10.	Temperature.	AgCl retained per 100 grm. AgNO
	(a) AgNO	O_3 : Water = 2:1.	***
grin.	e.e.	° C.	grm.
.e .e	2.0	57	0.478
7 ·0	2.0	45	0.410
8.0	2.0	40	0 359
9.0	2.0	35	0.819
0' 11	2.0	30	0 .261
7 ·0	1.0	26	0 .205
10.0	1.0	22	0 143
10.0	4.0	65	0.572
10.0	5.0	86	0.715
	(b) AgNO	$\theta_3 : Water = 1 : 1.$	
5 %	1.0	94	0 .286
6.0	1.0	84	0.239
7 .0	1.0	75 .	0.205
8 '0	1.0	66	0.179
9.0	1.0	58	0 159
5 5	0.5	48	0.180
6.2	0.5	40	0.110
12.0	0.5	23	0.060
	(c) AgNC	0_3 : Water = 1:2.	•
6.0	0.5	104	0 ·120
7.0	0.5	92	0.103
8.0	0.5	85	0.090
10 0	0.5	78	0.072
12.0	0.5	61	0.080
8.0	0 .25	45	0.045
12.0	0.25	28	0.080

In Table II the volume of salt solution added to a given weight of silver nitrate is shown for each experiment; the volume of water used to dissolve the nitrate is not shown, as it is merely the difference between the volume of salt solution and the total volume of water required to make up the solution to the desired ratio $AgNO_3$: water = 2:1 or 1:1 or 1:2. Thus, in the first experiment shown in the table, the proportions are—

AgNO₃: Water: Salt solution. == 6 grm.: 1 c.c.: 2 c.c.

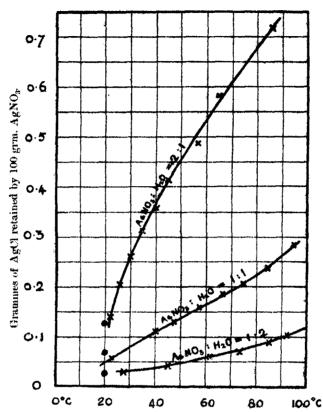


Fig. 2.—Influence of Temperature on the Solubility of Silver Chloride in Silver Nitrate Solutions.

The dots represent gravimetric experiments at 20° C.

These observations are plotted out in fig. 2. It will be seen that the solvent power of the strongest solution $(AgNO_3: water = 2:1)$ increases as the temperature rises, until at 86° no permanent precipitate is produced by adding silver nitrate (10 grm.) to decinormal salt solution (5 c.c.); the liquid may indeed be regarded as a decinormal solution of silver chloride, so far as the chloride and water are concerned. Silver nitrate is, therefore, a more effective solvent at high than at low temperatures.

In the weakest of the three solutions (AgNO₈: water = 1:2), change of temperature produces a similar effect since the solubility increases with rising temperature, but it does so at an increasing rate.

It might be expected that, at some intermediate concentration, an inflected curve would be obtained which would be concave in one range of temperatures and convex in another. This expectation is verified in the case of solutions in which the ratios are $AgNO_3$: water = 1:1. The observations from 20° to 70° plot out to a straight line which no doubt includes the point of

inflection; above 70° the curve rises like that for the weaker solution, below 20° it would probably show the curvature which is characteristic of the stronger solutions.

The volumetric readings are obtained with increasing difficulty as the temperature falls, but a comparison with the gravimetric readings, represented by black dots in fig. 2, shows that even at 20° there is no large difference between the two series.

Solubility of Silver Chloride in Common Salt.

The solubility of silver chloride in solutions of sodium chloride was determined gravimetrically at 15° C., by adding to a series of salt solutions (containing 28, 20, and 15 grm. NaCl per 100 grm. of solution) sufficient concentrated silver nitrate solution to produce rather more silver chloride than would remain dissolved. After warming and shaking, the solutions were left to stand during 24 hours at 15° C. A known weight of the clear solution was then diluted with water to 20 times its volume; the silver chloride which was precipitated was filtered off on a Gooch crucible, washed, dried, and weighed.

Volumetric determinations were also made of the solubility of silver chloride in 28, 20, and 15 per cent. salt solutions at temperatures up to the boiling points of the solutions. Decinormal silver nitrate solution was added from a burette to 20 c.c. of the salt solution; after every addition of silver nitrate the concentration of the salt was restored to its original

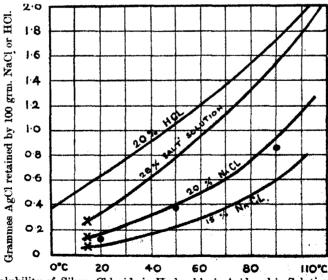


Fig. 3.—Solubility of Silver Chloride in Hydrochloric Acid and in Solutions of Common Salt.

Table III, Solubility of Silver Chloride in Solutions of Sodium Chloride.

	Gravimetric Measu	rements, 15° C.	
Strength of salt solution.	Weight of solution.	AgCl retained.	AgCl retained per 100 grm. NaCl.
*15 per cent. NaCl 20 , , ,, 28 ,, ,,	grm. 31 :674 * 37 :997 39 :117	grm. 0 '0030 0 '0104 0 '0305	grn. 0 ·068 0 ·134 0 ·279
	Volumetric Me	easurements.	P. F. C.
NaOl.	N/10 AgNO ₃ .	Opalescent at	AgCl retained per 100 grm. NaCl.
20 grm. of 15-per-cent, solution	c.e. 0·25 0·4 0·7 1·0 1·25	28 0 40 0 64 0 78 0 89 0	grm. 0 ·119 0 ·191 0 ·335 0 ·478 0 ·598
20 grm, of 20-per-cent. solution	1 · 7 0 · 43 0 · 65 0 · 82 1 · 2 1 · 6 2 · 12	102 · 5 17 · 0 26 · 0 87 · 0 51 · 5 67 · 0 79 · 5	0 · 812 0 · 156 0 · 284 0 · 295 0 · 430 0 · 524
20 grm, of 28-per-cent.	2 · 12 2 · 52 3 · 08 3 · 52 2 · 25	88 · 5 97 · 0 105 · 0	0·765 0·910 1·10 1·27
solution .	2·75 3·5 4·5 5·5 6·5 7·75	45 0 56 0 69 0 84 0 94 0 107 5	0 · 704 0 · 896 1 · 158 1 · 411 1 · 664 1 · 985

^{*} Grammes per 100 grm. of solution.

value by evaporating the solution until the meniscus reached a fixed mark on the wall of the test-tube. The solution was then allowed to cool slowly, with vigorous stirring, until it became opalescent.

The results of the gravimetric and volumetric measurements are given in Table III. It will be seen that the concentration of the silver chloride may be as great as 2 grm. per 100 grm. of salt, and that, in spite of its smaller solubility, common salt is a better solvent for silver chloride than is silver nitrate.

Fig. 3 shows that the data obtained by the two methods of measurement

are in satisfactory agreement. Three points calculated from data given by Barlow, and represented by black dots in the figure, are seen to lie upon a curve of precisely similar form.

Solubility of Silver Chloride in Hydrochloric Acid.

Hydrochloric acid of constant boiling point (20.24 per cent. HCl) was used, in order that loss by evaporation should not alter the strength of the acid. To 20 grm. of this acid silver nitrate solution was added gradually. For every cubic centimetre of solution added, 1.54 grm. (or 1.315 c.c.) of 33 per cent. HCl was also added, and the volume was then brought back to its original value by evaporating. The concentration of the acid was thus maintained at 20 per cent. by weight.

Table IV.—Solubility of	Silver Chloride	in 20-per-cent.	Hydrochloric Acid.
•		-	

HC1.	N/10 AgNO ₈ .	Opulescent at	AgCl to 100 grm. anhydrous HCl.
	o.e.	° C.	grm.
0 grm. of 20-per-cent.	1 0		
acid	1 • 1	0.0	0 .35
1	2.0	29 · 5	0 · 72
	8 •0	51 '5	1 .076
	8 .75	70.0	1 .846
į.	4 .25	82.0	1 .525
1	4 '75	90.0	1 .74
i	5 .80	107 0	2.08

It will be seen that the maximum amount of silver chloride dissolved is practically the same for hydrogen chloride and for sodium chloride, namely, 2 grm. AgCl per 100 grm. HCl or NaCl; the temperature of saturation was approximately 107° in each case; the concentrations were 20 per cent. HCl (saturated with gas at the boiling point), 28 per cent. NaCl (saturated with solid).

B. SILVER BROMIDE, IODIDE, AND SULPHIDE.

(With R. G. Parker, B.Sc.)

In the case of the bromide, iodide, and sulphide, the measurements of solubility are complicated by the formation of double salts. Thus the addition of potassium iodide to aqueous silver nitrate may result in the precipitation of

- (I) Silver iodide, AgI.
- (II) The double salt, AgI, AgNO₃.
- (III) The double salt, AgI,2AgNO₃.

So also by the action of sulphuretted hydrogen on aqueous silver nitrate there may be produced

- (I) Silver sulphide, Ag₂S.
- (II) The double salt, Ag₂S,AgNO₃.

The existence of double salts of silver iodide and silver nitrate was referred to as long ago as 1839 by Preuss.* Schnauss† and Kremer‡ prepared and analysed the salt AgI,AgNO₃. Weltzien§ and Rissell prepared and analysed the double salt AgI,2AgNO₃. Both salts were prepared and analysed a few years later by Stürenberg. Kremer** and Risse (loc. cit.) also prepared and analysed a bromide-nitrate of the formula AgBr,AgNO₃. Risse attempted further to prepare a chloride-nitrate, but only succeeded in obtaining a product having the composition AgCl,18AgNO₃, which he hesitated to regard as a definite compound.

The yellow sulphide-nitrate, Ag₂S,AgNO₃, which is formed when sulphuretted hydrogen is added to concentrated solutions of silver nitrate, was prepared and analysed by Poleck and Thümmel.†† Gutzeit‡ had put forward as a test for arsenic the formation of a yellow stain by the action of arseniuretted hydrogen on a filter-paper moistened with a concentrated solution of silver nitrate; this yellow stain became black on the addition of water. Poleck and Thümmel showed that identical phenomena are observed with SH₂, PH₃, AsH₃, and SbH₃. The compounds formed by the action of phosphoretted, arseniuretted, and antimoniuretted hydrogen have the formulæ

Ag₃P,3AgNO₃, Ag₃As,3AgNO₃, Ag₃Sb,3AgNO₃,

and are rapidly decomposed by water according to equations such as

$$Ag_8As_3AgNO_3 + 3H_2O = H_3AsO_8 + 3HNO_8 + 6Ag_8$$

The sulphide-nitrate, Ag₂S,AgNO₃, is much more stable, but decomposes directly into silver sulphide and silver nitrate when boiled with water.

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* 'Aun. d. Pharm.,' vol. 29, p. 329 (1839).

+ 'Archiv d. Pharm.,' 2, vol. 82, p. 260 (1855).

† 'Journ. für Prakt. Chem.,' vol. 71, p. 54 (1857).

§ 'Ann. Chem. Pharm.,' vol. 95, p. 227 (1855).

| 'Ann. Chem. Pharm.,' vol. 111, p. 41 (1859).

¶ 'Arch. d. Pharm.,' 2, vol. 143, pp. 12-19 (1870).

** 'Pogg. Ann.,' vol. 92, p. 49 (1854).

†† 'Ber.,' vol. 16, p. 2435 (1883).

‡‡ 'Pharm. Zeit.,' 1879, p. 263.
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^{§§} Compare Vitali, 'L'Orosi,' 1692, pp. 397-411; 'Chem. Soc. Abstr.,' vol. 2, p. 206 (1893).

Solubility of Silver Bromide in Silver Nitrate Solutions.

Volumetric measurements were made for a series of different concentrations, using the same method as in the case of silver chloride in aqueous salt solutions. Possibly on account of complications due to the formation of a bromide-nitrate, the volumetric and gravimetric measurements agreed less closely than in the case of the chloride. Only two of the six series of measurements are reproduced, therefore, in Table V and in fig. 4.

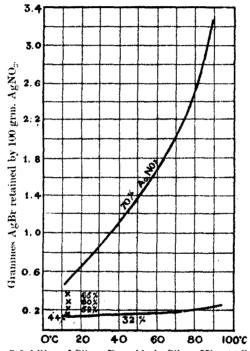


Fig. 4.—Solubility of Silver Bromide in Silver Nitrate Solutions.

Gravimetric measurements were made of the solubility at *14.5° C. of silver bromide in silver nitrate solutions containing 44, 52, 60, and 65 per cent. AgNO₃. In each case a clear solution, saturated with AgBr, was precipitated by dilution, and the silver bromide thrown down was collected and weighed. In one case a duplicate measurement was made by adding a known volume of N/10 KBr solution to a known weight of silver nitrate and weighing the silver bromide which remained undissolved. The two measurements showed a satisfactory agreement.

Table V shows that the solubility of silver bromide in silver nitrate solutions is much greater than that of silver chloride—on the average about three or four times as great. This is contrary to two isolated observations

by Hellwig,* who found that 100 c.c. 3N AgNO₃ (141·4 grm. of 36·1-per-cent. solution) dissolved 0·04 grm. of AgBr but 0·08 grm. of AgCl at 25·2° C.; our data, which formed part of a continuous series of observations, and are based both on volumetric and on gravimetric measurements, would give about 0·066 and 0·015 grm. respectively; it appears probable, therefore, that Hellwig has greatly over estimated the solubility of silver chloride in solutions of silver nitrate; on the other hand, his values for the solubility of silver bromide are of the same order of magnitude as ours.

Table V.—Solubility of Silver Bromide in Silver Nitrate Solutions,

(a) Volumetric Measurements.						
Silver nitrate.	KBr N/10.	Opalescent.	AgBr retained per 100 grm. AgNO ₈ .			
	c.o.	°C.	grin.			
[]	0 .65	22	0.129			
	0·72 0·8	35 44	0 ·144 0 ·159			
10 grm. made up to 82 grm.	0.8	62	0.178			
per 100 grm. of solution	1.0	67	0.188			
11	î · Ĭ	77	0.207			
i e	ĵ ·2	79	0.226			
};	6.0	87	1.13			
i]	8.0	53	1.50			
\$ [10.0	67	1 .88			
10 4. 70	11 .25	72	2 ·12			
10 grm. made up to 70 grm.	12.0	74	2 .26			
per 100 grm. of solution	12 .75	79	2 ·40			
11	18 5	82	2 .54			
1 }	15 .2	85.5	2 .92			
į į	17 '5	90	8 ·29			

(b) Gravimetric Measurements at 14.5° C.

AgNO ₃ .	Water.	Strength of AgNO ₃ .	AgBr retained.	AgBr retained per 100 grm. AgNO ₃ .
grm.	o.o.	per cent.	grm.	grm.
7 '826	9 ·32	44	0 ·0105	0 ·144
8 '29	7 ·65	52	0 ·0153	0 ·185
7 '255	4 ·84	60	0 ·0205	0 ·283 (0 ·299*)
7 '86	8 ·95	65	0 ·0268	0 ·365

^{*} By second method.

Solubility of Silver Iodide in Silver Nitrate Solutions.

Silver iodide dissolves in silver nitrate solutions even more readily than the bromide; but as the liquid may be saturated with three different solids,

* 'Zeitechr. Anorg. Chem.,' vol. 25, pp. 176-177 (1900).

namely AgI, AgI,AgNO₃, and AgI,2AgNO₃, no attempt was made to determine systematically the point of saturation under different experimental conditions. A complete series of solubility measurements has, however, been given by Hellwig* for a temperature of 25·2°.

By warming together at $60-70^{\circ}$ C., 2 grm. silver nitrate, 2 c.c. water, and 4 c.c. N/10 KI solution, a clear solution can be obtained. When heated to 100° it gave a yellow precipitate of pure silver iodide, which dissolved again when the liquid was allowed to cool slowly, with constant shaking, to $60-65^{\circ}$ C. Evidently, therefore, the silver iodide, which separates from a 25-per-cent. solution of silver nitrate at temperatures near the boiling point, is less soluble at 100° than at 70° C.

On allowing this solution to cool further it became cloudy at 50° C., and at 35° deposited white needles of the iodide-nitrate, AgI,AgNO₈. These needles were at once converted into the yellow iodide by contact with water and were also decomposed by alcohol. By draining and pressing on porous earthenware, a pure white powder was obtained, which lost only 0·1 per cent. when dried at 100° during 30 minutes, and therefore contained very little mother-liquor. When boiled with water during several hours, 0·0847 grm. gave 0·0506 grm. AgI and 0·0340 grm. AgNO₃, whence AgI: AgNO₃ = 1·07: 1, agreeing satisfactorily with the formula AgI,AgNO₃.

When this material was allowed to stand in contact with the mother-liquor for 12 hours at atmospheric temperature, the white needles changed completely into compact crystals of the iodide-nitrate, AgI,2AgNO₃. These were dried between filter-papers and then in a steam oven. After boiling with water during 5 hours, 0·1647 grm. gave 0·0679 grm. AgI and 0·0968 grm. AgNO₃, whence AgI: AgNO₃ = 1:1·97, agreeing closely with the formula AgI,2AgNO₃.

The observations recorded above show that the solubility of silver iodide in 25-per-cent, aqueous silver uitrate reaches a maximum at about 60°, and that at the point of maximum solubility the quantity dissolved even in this weak solution amounts to about 5 grm. AgI per 100 grm. AgNO₃. The iodide is thus about 30 times more soluble than the bromide and about 100 times more soluble than the chloride.

Solubility of Silver Sulphide in Silver Nitrate Solutions.

The first effect of adding sulphuretted hydrogen (or a soluble sulphide) to an aqueous solution of silver nitrate is probably in every case to precipitate the black sulphide Ag₂S. But, if the silver nitrate solution is at all concentrated, this soon changes over into the yellow sulphide-nitrate of the formula

Ag₂S,AgNO₃. The time required for the change from black to yellow to take place was found to be as follows:—

AgNO ₃ .	Water.	Change to yellow in
grm.	0.6.	
1	1	Less than 5 seconds
1	1 .2	5 seconds.
1	2	44 to 5 minutes.
1	8	11 to 2 hours.
1	4	12 hours.
1	5	5 days.
1	6	Several weeks.
ī	7	Several months.
ī	Ř	
1	9	Remained black.
ī	10))))

Table VI.—Conversion of Black to Yellow Silver Sulphide.

These numbers, which are plotted out in fig. 5, indicate that the black sulphide would probably be permanent in contact with solutions containing 10 per cent. AgNO₃ or less.

There is evidently a limiting concentration of silver nitrate above which the yellow sulphide-nitrate would be stable, whilst below it the black

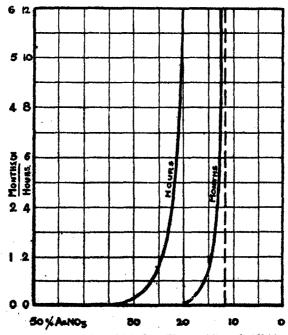


Fig. 5.—Conversion of Black to Yellow Silver Sulphide.

sulphide would be stable. In order to determine the limiting concentration more accurately, attempts were made to measure the velocity of the converse change from yellow to black at different concentrations: these were not successful, as the change is both slow and indefinite. It was found, however, that in contact with 1-per-cent. AgNO₃ the yellow double salt became black in the course of 12 hours.

The yellow salt was prepared by adding to 10 grm. of dry silver nitrate a solution of 1.5 grm. Na₂S in 5 c.c. of water. The yellow precipitate was drained on a small Buchner funnel and washed with alcohol until no silver could be detected in the washings. It was then rinsed with ether and allowed to dry in the dark. Qualitative analysis showed that the substance contained only silver, sulphide, and nitrate. Gravimetric estimation of the silver gave

Ag = 77.05, 77.02 per cent. $Ag_2S, AgNO_3$ requires 77.49 per cent.

When boiled with water 0.2054 grm. gave a residue of silver sulphide weighing 0.1215 grm. (calc. 0.1218) and containing 87.2 per cent. Ag (calc. 87.15 per cent.); the extract contained 0.0835 AgNO₃ (calc. 0.0836); the ratio $AgNO_3$: $Ag_2S = 1.002$: 1 agrees closely with the formula Ag_2S , $AgNO_3$.

As the sulphide-nitrate is the stable form at all concentrations above 10 per cent., all the solubility measurements are for solutions saturated with this form of the sulphide, although the data are worked out for the simple sulphide Ag₂S. Some preliminary experiments were made with sulphuretted hydrogen, purified by dissolving in milk of magnesia and decomposing the resulting sulphide solution by boiling. The purified gas was dissolved in boiled water and estimated (1) by precipitating as Ag₂S and as CdS, and (2) by titration with iodine; but it escaped so quickly from the solution that it could not be used conveniently for the solubility measurements. Instead, Kahlbaum's purest crystalline sodium sulphide was used, in freshly prepared solutions which were standardised by titration with iodine

$$Na_2S + I_2 = 2NaI + S.$$

The solubility of silver sulphide in silver nitrate solutions was determined

- (a) Gravimetrically at 15°.
- (b) Volumetrically at 100°.

The volumetric method could not be used in the same way as in the case of the chloride and bromide, because the solubility of the sulphide is almost independent of the temperature; nor could the method used at 100° be used at atmospheric temperature, since silver sulphide when once precipitated is

very difficult to dissolve again, especially at temperatures below the boiling-point.

The gravimetric measurements were made by adding 50 c.c. $0.948 \times N/5$ sodium sulphide to 100 grm. of silver nitrate (AgNO₃: water = 2:1) warming and stirring thoroughly, then leaving 24 hours to settle at the atmospheric temperature. The undissolved silver sulphide was filtered off, drained, washed with alcohol and ether, and weighed as Ag₂S,AgNO₃. This process was repeated after adding successive quantities of 50 c.c. of water to the solution until all the sulphide had been precipitated. The solubilities are much less even than in the case of the chloride, and are therefore subject to larger percentage errors. A further source of error is introduced by the difficulty of weighing the double salt, which decomposes if washed with water; thus the actual weight of the double salt collected was 2.040 grm., the calculated quantity being 1.985 grm. The data are set out in Table VII.

AgNO _s .	Water.	Ag ₂ S, AgNO ₃ precipitate.	Ag ₂ S retained* per 100 grm, AgNO ₃ ,	Strength of $AgNO_3$.
grm.	c.c.	grm.	grni.	per cent.
100	50 †	1 924	0.0696	66 7
100	100	0.0789	0 .0227	50.0
100	150	0.0220	0.0097	40 .0
100	200	0.0163	trace	38 ·3
100	250	trace	0.0	28 .6

Table VII.—Solubility of Silver Sulphide in Silver Nitrate Solution at 15° C.

Volumetric measurements were made at 100° C. by two methods. In the first a solution of sodium sulphide was added to 10 grm. of silver nitrate, mixed with a variable quantity of water, with constant shaking in a closed test-tube, until a faint permanent precipitate was formed. In the second method a definite quantity of sodium sulphide was added to a solution of silver nitrate under such conditions that a clear solution was produced; water was then added gradually until a faint permanent precipitate was formed. The second method gives better results than the first; the results obtained by both methods are collected in Table VIII.

It will be seen at once that even at 100° C. the quantities of silver sulphide retained are very small; at the high concentration AgNO₈: water = 2:1 the quantity of silver sulphide is only about 0.1 per cent. of the weight of silver nitrate in the solution. The order of magnitude is the same at 100° C. as

^{*} Calculated from the total weight of sulphide-nitrate precipitate on dilution.

[†] Containing Na S of concentration 0 948 N/5 or M/10.

Table VIII.—Solubility of Silver Sulphide in Silver Nitrate Solutions at 100° C.

AgNO _s .	Na ₂ S.	Water.	Ag ₂ S retained per 100 grm. AgNO ₃ .	Strength of AgNO ₃ .
<u>-</u>	(a) First Me	thod.	
grm.	c.c.	j o.c.	grm.	per cent.
10	1·1 N	0.0	1.36	90.2
10	1 4 N/2	0.0	0 .87	87 •7
10	2·15 N/5	0.0	0 .62	82 ·2
10	2.6 1.047 N/10	0.0	0.348	79 4
10 :	2 ·1 ,,	1.0	0 -281	76 .8
10 .	1.1 ,,	2.5	0.147	78 .2
10	0.45 ,,	5.0	0.000	64 7
	(b)	Second M	ethod.	
10	2 ·0 0 ·98 N/10	1 .2	0 243	74 0
10	1.5 ,,	2.6	0.180	70.9
10	1.0 ,,	4 ·15	0 ·120	66 0
10	0.5 ,,	6 .15	0.080	60 ·1
10	0 •2 ,,	8.5	0.024	58 .2
10	0.1 ",	11 '5	0.012	46 '5
10	0.05 ,,	14.5	0.008	40.8

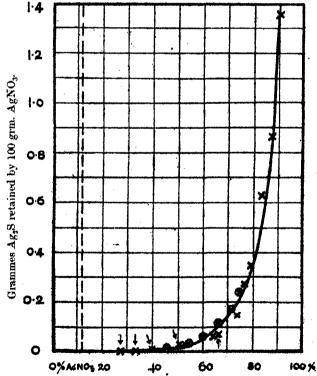


Fig. 6.—Solubility of Silver Sulphide in Silver Nitrate Solutions.

Gravimetric measurements at 15° are indicated by arrows; the other points indicate volumetric measurements made at 100° by two methods.

at 15° C. for similar concentrations, but by using concentrations up to $AgNO_3$: water = 9:1 the solubility of the sulphide in the hot solutions was increased to 1:36 per cent. of the weight of silver nitrate. These concentrated solutions are a clear yellow, resembling aqueous solutions of potassium chromate.

The data now given can only be regarded as approximate, but the general influence of the concentration of the silver nitrate on the solubility of silver sulphide is shown clearly in fig. 6, in which all the data are set out together, and are seen to be very near to a smooth curve whether they refer to a temperature of 15° or 100° C.

Fog Signals.—Areas of Silence and Greatest Range of Sound.

By A. Mallock, F.R.S.

(Received June 19,-Read June 25, 1914.)

The experience of Trinity House in regard to the audibility of sound signals has brought to notice the fact that on occasions the sound may be heard near the source and again at a considerable distance, while inaudible between these positions.

This was first observed, or at least prominently brought forward, by Prof. Tyndall. The statement was regarded with some scepticism by scientific men at the time, but the explanation of the effect of wind on sound given by Prof. G. Stokes* will, with a little amplification, suffice also for the silent areas. Stokes in this explanation (which was repeated by Henry† and by Osborne Reynolds‡) points out that the speed of the wind, in consequence of the surface friction of the ground, increases with the height, and that since the velocity of sound is constant not with reference to the ground, but to the air through which the sound travels, the front of a plane wave vertical at some given instant will subsequently lean backwards if travelling against the wind, and forwards if with the wind. Or, in other words, the sound tends to leave the ground in the first case and to cling to it in the second.

If one may use such a word as a "ray" in connection with sound, the ray to windward is deflected upwards, and the ray to leeward, downwards. The

^{*} Stokes, 'Brit. Assoc.,' Dublin, 1857.

[†] Henry, "Researches in Sound," 'Annual Report of the U.S.A. Lighthouse Board,' 1865.

¹ Osborne Reynolds, ' Roy. Soc. Proc.,' April 25, 1874.

actual velocity of the wind has only a small effect in either case (of the order of the ratio of the speed of the wind to that of sound), the operative cause being the velocity gradient.

In the case of regions of silence, on both sides of which the same sound can be heard, all that has to be accounted for is how a sound ray can form, as it were, an arch over the silent region.

This can evidently happen if the velocity gradients in the wind change sign at appropriate levels, and it is a very simple calculation (given later) to determine what gradients are required in order that a ray (i.e. the normal to the wave-front) shall follow a harmonic curve of given amplitude and wavelength.*

The fact that areas of silence are (though not actually rare) not common, points to somewhat exceptional conditions being required for their development. The presence of reversed wind-gradients at comparatively low levels also occurs, it may be said (there is not much detailed information on the subject), with the same order of frequency, and if the two phenomena were found to be always or generally present together, the suggested explanation would receive some confirmation[†]); but, as is well known, variation of wind velocity is not the only cause of deviation in a sound ray: anything which causes variation of velocity in different parts of the wave-front will have a like effect.

The velocity of sound is proportional, among other things, to the square root of the absolute temperature, and in fact a temperature change of 1° C. corresponds to nearly 2 feet per second change of velocity.

As a rule, the temperature of the atmosphere falls as the altitude increases, so that, as a rule also, all sound rays which start horizontally from a source near the ground are deflected upwards, whatever may be their azimuthal direction, and it is probably owing to this that, even on calm days, intense sounds are audible at sea to such very moderate distances.

Lord Rayleigh has pointed out (taking into account the energy which is known to be put into sound waves emitted by some of the coast fog signals, and the smallness of the wave amplitude which is known to be audible) that were it not for some extraneous cause such signals would be heard at distances exceeding 1800 miles, instead of the 10 or 12 which experience shows to be the usual limit.

^{*} Since this paper was written I find that Lord Rayleigh, in the second edition of 'The Theory of Sound' (which I had not seen), has given (vol. 2, p. 134) the differential equation of the path of a sound ray when the wind velocity is continuously variable.—Oct. 19, 1914.

[†] There would be no great difficulty in observing this by the aid of pilot balloons.

At certain times, however, reversals of the temperature gradient are to be met with, especially in the evening, when the air next the ground is cooled by radiation, and thus forms a pond of cold air under a warmer layer. In such cases the effect on sound in all azimuths is of the same kind as that observed to leeward of a source when the wind velocity increases with the height. This has been given as a probable explanation of the increased audibility of sounds at night.

To consider these points quantitatively, suppose that it is required to find the distribution of wind velocity at various elevations which will cause a ray of sound to follow a simple harmonic curve of assigned wave-length and amplitude. The wind is assumed to be horizontal and constant at each altitude, but to vary with the altitude. Since the ray is to follow a curved path, the wave-front must contain the radius of curvature, and, in fact, the wave-front may be considered as if it were a flat plate attached to the radius of curvature.

Consider a ray which starts horizontally at ground level, and let its assigned path be $y = h(1-\cos px)$ (x horizontal, y vertical), where h is the assigned amplitude and $p = 2\pi/\lambda$. If a and v are the velocities of sound and of the wind respectively, the velocity of the wave-front is $a \pm v$, and the velocity gradient dv/dy = a/R. For a harmonic curve where the amplitude is small compared to the wave-length, $R = 1/d^2y/dx^2$. Hence

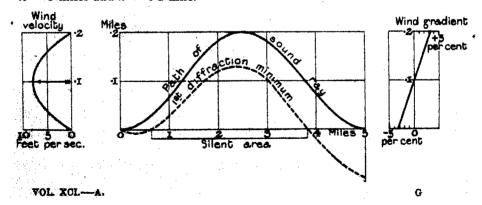
$$dv/dy = ahp^2 \cos px = ap^2(h-y).$$

Put $(h-y) = \eta$ and let it be a condition that the wind velocity is zero at ground level (y = 0). Then the velocity gradient is

$$-ap^2\eta$$
, (1)

$$v = \frac{2\pi^3\alpha}{\lambda^3}(h^2 - \eta^2). \tag{2}$$

Diagram 1 shows these results graphically for a harmonic curve for which $\lambda = 5$ miles and h = 0.1 mile.



The wind velocity is a maximum at h, and there reaches 805 feet per second. Above this it dies out again to a calm at 2h. The velocity differences are the ordinates of a parabola whose axis is the line y = h. The path of the ray will not, of course, be the actual boundary of the sound, as the latter will spread by diffraction into the space between the path and the surface of the ground. The distance below the path to which the sound is audible will depend on the wave-length of the note employed, but the smaller the wave-length the more rapid will be the transition from sound to silence.

If the diffraction of sound is treated in the same way as diffraction of plane waves of light passing the edge of a screen (and for such small curvatures as are considered the method is applicable as an approximation) the first minimum, at distance x from the source, occurs at $\sqrt{(2x\lambda)}$ from the geometrical path.

The wave-lengths emitted by fog syrens are of the order of 6 feet or, say 0.001 mile. Thus at 5 miles the sound would be just inaudible (or, rather, would pass through a minimum) at $(10 \times 0.001)^{\frac{1}{2}} = 0.1$ mile, that is between 500 and 600 feet below the harmonic curve.

The boundary of silence is shown in the diagram by the dotted line. It would appear, then, that in the example given there would be a silent area to windward about 3 miles wide, beginning at 3 mile from the source of sound.

In the example it has been supposed that the temperature was everywhere constant, but in normal conditions the temperature of the atmosphere near the earth's surface falls with the height at the rate of about 10° C. per mile, and in consequence, as has been observed by Stokes and others, the direction of a sound proceeding horizontally is gradually directed upwards.

A difference of temperature of 10° C. lowers the velocity of sound by about 20 feet per second. Hence a plane wave will advance as if it were carried by a radius 55 miles long, and if the diffraction effect is estimated as before, a sound ray which starts horizontally from x = 0 and follows a circle of 55 miles radius may be expected to be inaudible, whatever its initial loudness, when the distance of the circle from the ground is $\sqrt{(2x\lambda)}$; that is, when $x^2/2R = \sqrt{(2x\lambda)}$, or $x = 2R^{i}\lambda^{i}$, so that, if $\lambda = 0.001$ mile and R = 55

x = 8 miles nearly.*

This cannot be said to disagree greatly with experience. Many cases are recorded in which the sound is inaudible at less than 8 miles, and many also

^{*} Even if \(\) was the greatest wave-length recognisable as sound this distance would be only doubled.

where the range is much greater, but at any rate this is the order of distance to which a sound generated near the ground level can be heard at the same level in still air with the normal temperature gradient.

On the whole, it is the audibility of distant sounds rather than the reverse which requires explanation, but the known velocity gradients and changes of temperature at various levels seem amply sufficient for the purpose.

Sounds which have their origin at a considerable height can be heard at greater distances. Thunder, for instance, is occasionally heard when the flash which gives rise to it does not even show on the horizon, and this would indicate a distance of the order of 50 to 100 miles.

The phenomena of the deviation of sound rays present a considerable analogy to mirage, wind and temperature gradients taking the place of variation of refractive index.

Many interesting experiments on the propagation of sound under various conditions still await trial, but such experiments could only be undertaken by a government, or at any rate would be very costly if carried out privately. They could not be made on English coasts or where they might interfere with navigation,* but there are many small islands in lonely seas in various latitudes which, at various times of the year, would be appropriate for the purpose.

^{*} This refers chiefly to experiments at night.

Quantitative Measurements of the Absorption of Light. I.—The Molecular Extinctions of the Saturated Aliphatic Ketones.

By Francis Owen Rice, 1851 Exhibition Scholar in the University of Liverpool.

(Communicated by Prof. E. C. C. Baly, F.R.S. Received October 2, 1914.)

The results of an examination of the absorption spectra of some saturated aliphatic ketones in alcoholic solution were published by Stewart and Baly,* and it was shown that there seemed to be a direct connection between the persistence of the absorption band and the chemical reactivity of the ketone in each case as measured by the rate of the formation of its oxime or sodium bisulphite compound. Since the date of that paper the technique of absorption methods has been considerably improved, and it appeared worth while to investigate the absorptive power of the same ketones with the more efficient methods now available.

It was found at once that there is a very considerable difference in the position of the absorption band according to whether the ketone is observed in the pure state or in solution. As is well known, the effect of the solvent generally is to shift the absorption maximum towards the longer wavelengths, this shift being as much as 100 Å.U. in the case of acctone and its aqueous solution. Moreover, it was also found that the shift varies irregularly from ketone to ketone, and it is therefore obvious that in order to compare the ketones amongst themselves it is necessary to deal with the pure ketones and not their solutions.

The only results that have been published of the absorptive power of the pure homogeneous ketones are those by Bielecki and Henri,† and by Purvis and McClelland.‡ In the first paper is given the absorptive power of pure acetone as determined by the well-known method of these authors, and, indeed, this is the only quantitative observation of the absorptive power of a pure saturated aliphatic ketone that has been published.

Purvis and McClelland state that in the case of diethyl ketone a layer. 0.8 mm, thick with one minute exposure shows complete absorption of all the rays between $\lambda = 3050$ and $\lambda = 2420$, and of all the rays beyond $\lambda = 2280$. I find that with Kahlbaum's material once redistilled and a layer 0.5 mm.

^{* &#}x27;Trans, Chem. Soc.,' vol. 89, p. 489 (1906).

^{† &#}x27;Ber.,' vol. 46, p. 3627 (1913).

^{† &#}x27;Trans. Chem. Soc.,' vol. 101, p. 1810 (1912).

thick, the limits of absorption are $\lambda = 3050$, 2415, and 2290. These two results are in good agreement.

A general theory as regards the presence of absorption bands was put forward by Hartley, who postulated that they are due to molecular vibrations of a frequency comparable with that of light. This theory has been recently revived in a somewhat modified form by Hantzsch, and by Henderson and Heilbron. It is suggested that intramolecular vibrations take place, and that these give rise to electronic vibrations which form the origin of selective light absorption. If this theory were true it would be expected that the effect of substitution of the hydrogen atoms of acetone by alkyl groups would very considerably modify the absorptive power exerted. If the origin of the absorption is to be traced to the molecular vibrations, then surely great differences would be found between the absorptive power, for example, of acetone and pinacoline, or of acetone and methyl nonyl ketone.

On the other hand, from an extended investigation of the absorption spectra of certain groups of organic compounds, it has been shown that the molecular vibration theory is unsound, a conclusion that is strongly supported by the results published by Henri and his colleagues from their work upon the relation between the photochemical action of light on the ketones and their absorptive power. It has been shown that the origin of selective absorption of light by organic compounds would seem to be in the electromagnetic field surrounding the molecules, and that the light in being absorbed does work upon these fields and establishes a photodynamic equilibrium. Whereas the molecular vibration theory attributes the phenomenon of absorption to optical resonance, the electromagnetic force field theory attributes the absorption to the fact that the light does work upon the closed or partially closed electromagnetic fields. As has been previously shown, the latter theory affords an explanation of fluorescence and phosphorescence and at the same time establishes a direct relation between light absorption and chemical reactivity, which the molecular vibration theory entirely fails to do.§

The application of the electromagnetic force field theory to the saturated aliphatic ketones enables certain deductions to be made as to the absorptive power of these compounds, and of these deductions every one has been confirmed by experiment. According to this view the origin of the absorption lies in the electromagnetic field surrounding the molecule as a whole.

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* 'Ber.,' vol. 43, p. 3049 (1910).
† 'Roy. Soc. Proc.,' A, vol. 69, p. 414 (1913).
‡ Baly and Rice, 'Trans. Chem. Soc.,' vol. 101, p. 1475 (1912).
§ Baly, 'Phys. Zeit.,' vol. 14, p. 893 (1913); 'Phil. Mag.,' vol. 27, p. 632 (1914).
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This field has its principal origin in the carbonyl group, and can only slightly be modified by the adjacent alkyl groups. Four important deductions at once follow as regards the absorption of these ketones.

Firstly, the substitution of hydrogen atoms near the carbonyl group by means of alkyl groups would only alter slightly the nature of the force field with the result that the wave-length of the light absorbed would slightly be altered.

Secondly, a similar effect would be produced by dissolving the ketone in a solvent.

Thirdly, the substitution of a hydrogen atom by an alkyl group would have a smaller effect the farther removed the hydrogen atom is from the carbonyl group. The effect of substitution would be vanishingly small when the side chain of the ketone has reached a certain length.

Fourthly, the molecular absorptive power of all the ketones should be the same, that is to say, equal numbers of molecules of all the ketones should absorb the same quantity of light provided that the ketones are monomolecular and not associated.

As already stated, these deductions from the theory have all been experimentally confirmed.

When the present investigation was finished a second paper was published by Henderson and Heilbron, in which they suggested a method for putting their theory to a crucial test. In hexamethylacetone,

there are no hydrogen atoms immediately adjacent to the carbonyl group, and therefore this compound cannot undergo any change in chemical structure such as is postulated by these authors as the basis of absorption. This compound, according to their view, therefore should not show any selective absorption, and in their paper Henderson and Heilbron stated that they had examined this substance and found that it possessed no trace of selective absorption. According to the electromagnetic force field theory, it is obvious on the other hand that this compound should show selective absorption. Owing to the substitution of all the hydrogen atoms of acetone by methyl groups, the absorption band should only be altered in position, while the molecular absorptive power should be the same as that of all the other ketones.

Henderson and Heilbron do not give any details as to the preparation and purification of the hexamethylacetone as used by them, and owing to the essential importance of their observation it was thought advisable to repeat their examination of this compound. A considerable quantity was therefore prepared and purified in the manner described below. It was then found to exhibit a strong absorption band in the expected position, and also to possess exactly the same molecular absorptive power as all the other ketones examined. This result makes Henderson and Heilbron's theory that the absorption is connected with a change in chemical configuration quite untenable, and seems in a very marked manner to confirm the view that the origin of the absorption lies in the electromagnetic field of the CO group as modified by the adjacent carbon and hydrogen atoms. The mechanism of absorption cannot be dynamic in the sense that the hydrogen atoms are labile.

On commencing this investigation, some preliminary observations showed that the ketones varied most irregularly amongst themselves as regards their absorptive power, and in this way, although the compounds had been fractionally distilled in vacuo with the greatest care and only the middle fraction used, doubt was thrown on their purity. It was further found that in treating the fractions with a dilute neutral solution of potassium permanganate an immediate reduction of the permanganate took place, thus proving that impurities were present. It was not found possible to purify any of the ketones by distillation alone, and chemical methods were employed in each case. It follows from this that all the results that have been published of the absorption by the ketones are vitiated by the fact that the ketones were not examined in a state of absolute purity, with the exception of Bielecki and Henri's measurement of acetone already referred to.

When by suitable means the pure ketones are prepared, a striking difference is at once noticed between the absorption curves before and after purification. The absorption curve, such as has been published by previous authors, is represented as having an absorption minimum on the ultra-violet side of the band, the absorption increasing on either side of this minimum. After purification this minimum disappears and the ketone becomes diactinic in this region. This is well shown in fig. 1, which gives the qualitative absorption curves of ethyl propyl ketone before and after purification.

It is obvious from this that the absorption minimum shown before purification is due to the presence of impurities, the general absorption of which is superposed upon the selective absorption of the pure ketone. An important point arises in connection with the presence of an impurity in the ketone. The absorptive power of these compounds is relatively very small compared with that of ring compounds. Consequently, the presence of such impurity, even in small amounts, would vitiate any quantitative measurement of the absorptive power of an aliphatic ketone. It is well known how readily

ketones, especially those containing the acetyl group, are converted into cyclic compounds, and therefore the rigid absence of such impurities is

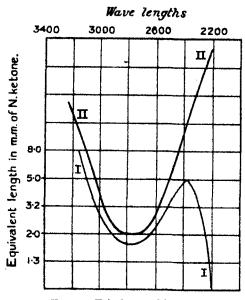


Fig. 1.—Ethyl propyl ketone.

I. Distilled in vacuo.

II. Purified through semicarbazone.

absolutely essential. It was evident therefore that before any reliable measurements of the ketones could be made it was absolutely necessary to prepare them in a state of purity.

The ketones used in this investigation were all purified with the greatest possible care, and no specimen was used for absorption measurements unless it showed itself to have no trace of an absorption minimum on the ultra-violet side of the absorption band, and to give no reduction of a dilute neutral solution of potassium permanganate when shaken with it for 15 minutes. When this was found to be the case the compound was considered to be optically pure.

The following methods were employed in the purification of the several ketones:—

Acetone.—Kahlbaum's material, prepared from the sodium bisulphite compound, was used after careful redistillation. The optical test mentioned above seemed to establish its purity, but in order to confirm this conclusion the acetone was treated according to the method described by Shipsey and Werner.* The absorptive power was not altered in the smallest degree by this treatment.

^{* &#}x27;Trans. Chem. Soc.,' vol. 103, p. 1255 (1913).

Methyl Ethyl Ketone, Methyl Propyl Ketone, Methyl iso-Propyl Ketone, Diethyl Ketone, Methyl Butyl Ketone, Methyl iso-Butyl Ketone, Methyl Hexyl Ketone, and Methyl Nonyl Ketone.—These ketones were all purified by conversion into the sodium bisulphite compound, from which the original ketone was regenerated. The ketone was shaken with an excess of a saturated solution of sodium bisulphite until the maximum possible yield of the addition compound had been formed. In the case of the higher ketones a little alcohol was added to increase the velocity of the combination. The mixture was filtered at 0° C. and the double compound thoroughly drained, washed once or twice with ether, and dried on a porous plate. The dried material was transferred to a flask containing a solution of sodium carbonate. The ketone was then, if possible, distilled off in a current of steam. With the higher boiling ketones this was found to be impossible, owing the formation of coloured impurities which could not be removed by any means. In these cases the steam was passed into the alkaline solution for just sufficient time to decompose the addition compound. The solution was then cooled and the ketone mechanically separated.

In the case of the lower boiling ketones which were distilled in a current of steam, the aqueous distillate was treated with potassium carbonate in order to salt out the ketone, which could then be mechanically separated. In every case the ketone was treated with a little alkali in order to remove any trace of sulphur dioxide or carbon dioxide.

The several ketones prepared in this way were dried for 48 hours over fused calcium chloride and then distilled. If the boiling point of the liquid were 100° or less, the distillation was carried out under ordinary pressure, but if the boiling points were above 100° the distillation was always carried out under reduced pressure.

Pinacoline.—This was purified by conversion into the oxime. This compound was prepared according to the method given by Lapworth and Steele.* The oxime, when thus obtained, was recrystallised from alcohol. It was then filtered and dried on a porous plate. The pure oxime was then transferred to a flask containing a 10-per-cent. aqueous solution of sulphuric acid and the pinacoline distilled over in a current of steam. A certain amount of undecomposed oxime was found to be carried over with the pinacoline. This was removed by shaking the ketone with a 15-per-cent. solution of sodium hydroxide, after which it was washed with water, dried, and distilled.

Ethyl Propyl Ketone, Dipropyl Ketone, and Ethyl iso-Butyl Ketone.—The first attempts to purify these compounds were made by means of their oximes, * 'Trans. Chem. Soc.,' vol. 99, p. 1882 (1911).

but this was found to be impracticable owing to the fact that the oximes are oils which would not crystallise, even at very low temperatures. The final method adopted was to convert these ketones into their semicarbazones, from which the pure substances were regenerated. The method of procedure was exactly similar to that used in the case of the oximes and described above for pinacoline.

A further purification was made of dipropyl ketone by recrystallising it from hexane at a temperature of -80° . For this purpose a special apparatus was devised to enable the crystals to be filtered off at the low temperature. It was found, however, that the ketone, after the recrystallisation, had identically the same absorptive power.

Hexamethylacetone.—This compound was prepared from pinacoline according to the method described by Haller and Bauer.* From 100 grm. of pinacoline about 60 grm. of the crude ketone boiling at 159–161° were obtained. Since this ketone does not form an oxime, semicarbazone, or hydrazone, the problem of its purification seemed to present some difficulty. A preliminary test showed that on shaking with potassium permanganate solution considerable reduction took place. The whole of the ketone was therefore shaken with successive portions of permanganate solution until no further reduction took place. The ketone was then washed with water, alkali, acid, and again with water. After drying the ketone was distilled with a Young fractionating column, and almost the whole quantity passed over at 161–161.5°. The absorption was then examined, and, as already mentioned, it was found to exert strong selective absorption and to possess the same molecular absorptive power as the other ketones.

In order to place its purity beyond question, the ketone was recrystallised from absolute methyl alcohol at -80° . The separated crystals, after melting, were washed with water, dried, and distilled under reduced pressure. The whole of it distilled at 61.5° at 15 mm. pressure. No change was made in the absorption by this treatment, and the purity of the ketone was thus established beyond any question.

The boiling points of the ketones are shown in the table on p. 83.

The preliminary part of this investigation was carried out with a large quartz spectrograph, the usual qualitative absorption curves being obtained. In order to obtain the requisite thin layers of the liquids, the micrometer cell as previously described was used.† This method of work was superseded by the spectrophotometric arrangement recently devised by the firm of Hilger and Co. With this apparatus it is possible to determine the extinc-

^{* &#}x27;Comptes Rendus,' vol. 150, p. 582 (1910).

^{† &#}x27;Baly and Rice, 'Trans. Chem. Soc.,' vol. 103, p. 91 (1913).

Ketone.	Boiling point.	Pressure
	•	mm.
Acetone	56 .3	759
Methyl ethyl ketone	80 1	758
Methyl propyl ketone	101 -5	759 2
Methyl isopropyl ketone	94 .7	756 .4
Methyl butyl ketone	125 -5	758 -8
Methyl isobutyl ketone	115 -8	759 -8
Pinacoline	106 .2	759 3
Methyl hexyl ketone	169 -5	758 9
Methyl hexyl ketone	65 · 2	12
Methyl nonyl ketone	99 ·1	12
Diethyl ketone	101 0	761 .5
Ethyl propyl ketone	128 .4	757 ·2
Dipropyl ketone	75 1	68
Hexamethylacetone	64 .5	1.5

tion coefficient to as far as 2100 Å.U. As a measure of the accuracy of this instrument it may be said that it has been found possible to find the position of maximum absorption, that is to say the optical centre of the absorption band, to within ± 3 Å.U.

The extinction coefficient, ϵ , is given by

$$\epsilon = \frac{1}{d} \log \frac{I_0}{I},$$

where I_0 is the intensity of the incident light, I the intensity of the emergent light, and d the thickness of the absorbing layer.

In order that the results be comparable it is necessary to take into account the molecular concentration of the ketone. If c be the normality of the ketone (Specific gravity × 1000/Molecular weight), the molecular extinction is given by M = e/c.

The molecular extinction curves are obtained by plotting the values of M on the ordinates against the corresponding wave-lengths on the abscissæ. Owing to the compactness of the spectrophotometric apparatus it was not found possible to use the micrometer cell, but a number of cells were made of known thicknesses by cementing together two plain parallel quartz plates together with a wire ring of known diameter between them.

The thickness of the two quartz plates being known, it was possible to measure the distance between them to within 0.003 mm. Several cells were made to hold liquid layers from 0.8 mm. to 2.0 mm., and found to be sufficient for all the ketones examined.

The extinction curves may be discussed from two points of view, namely, the optical centres of the absorption bands, and the molecular extinctions

at the centres. The wave-lengths of the centres of the absorption bands are given in the following table:—

Table I.

Acetone	2747	Methyl isopropyl ketone	2820
Methyl ethyl ketone	2770	Methyl isobutyl ketone	2810
Methyl propyl ketone	2790	Pinacoline	2850
Methyl butyl ketone	2790	Diethyl ketone	2780
Methyl hexyl ketone	2790	Ethyl propyl ketone	2800
Methyl nonyl ketone	2790	Dipropyl ketone	2820
• •		Ethyl isobutyl ketone	2820
		Hexamethylacetone	2950

The effect of substitution of the hydrogen atoms by CH₃ groups is shown in a very interesting manner in the above table. In the first column are given the values for the normal ketones containing the acetyl group, and as may be seen the substitution of an α -hydrogen atom in acetone to give methyl ethyl ketone, i.e. CH₃—CO—CH₃—CO—CH₂—CH₂—CH₃, causes a shift to the red of 23 Å.U. The substitution of a β -hydrogen atom in the latter, i.e. CH₃—CO—CH₂—CH₃—CO—CH₂—CH₃—cO—CH₂—CH₃, causes a further shift of 20 Å.U. Substitution of a γ -hydrogen atom makes no difference, and thus in methyl propyl ketone the limiting length of side chain has been reached. The general conclusion may be drawn, therefore, that all normal ketones having the formula CH₃—CO—CH₂—CH₂—R, where R is any saturated alkyl radical, have absorption bands with centre at $\lambda = 2790$ Å.U.

The substitution of a second a-hydrogen atom by CH₃, i.e.

$$CH_3$$
— CO — CH_2 — CH_3 \rightarrow CH_3 — CO — CH , CH_3

methyl isopropyl ketone, causes a shift of 50 Å.U., a much greater effect than that observed in the first substitution. This is doubtless due to the formation of the iso group, which will be referred to below. This exaltation due to the iso group is not evidenced when it is in the β -position for the substitution in methyl propyl ketone to give methyl isobutyl ketone, i.e.

$$CH_3$$
— CO — CH_2 — CH_3 — CH_3 — CO — CH_3 — CH_4 — CH_5

only gives the normal shift of 20 Å.U.

The substitution of the third α -hydrogen atom in methyl isopropyl ketone to give pinacoline, i.e.

$$\begin{array}{c} \mathrm{CH_3} \\ \mathrm{CH_3-CO-CH} \\ \downarrow \\ \mathrm{CH_3} \end{array} \rightarrow \begin{array}{c} \mathrm{CH_3-CO-C} \\ \mathrm{CH_3} \\ \mathrm{CH_3} \end{array}$$

causes a further shift of 30 Å.U.

The shifts obtained in the successive substitution of the three α -hydrogen atoms of acetone are 23, 50, and 30 Å.U. respectively.

The last five ketones show the effect of substitution on both sides of the carbonyl group, and, as may be seen, the same laws are obeyed, namely, that substitution in the α - and β -positions only causes a shift in the centre of the absorption band. The case of hexamethylacetone is peculiarly interesting. The substitution of the three α -hydrogen atoms in acetone by methyl to give pinacoline causes a shift of 103 Å.U., and therefore it is to be expected that the substitution of all six α -hydrogen atoms should cause a shift of twice this amount, i.e. 206 Å.U. The centre of the absorption band of hexamethylacetone should be at 2747 + 206 = 2953 Å.U. The observed value is 2950.

Turning now to the molecular extinction curves of the ketones, it may be pointed out that the curves of the ketones of the general formula CH_3 —CO— CH_2 — CH_2 —R, where R is any saturated alkyl radical, are all absolutely identical. Further than this, the extinction curves of all the remaining ketones, with the exception of acetone and methyl ethyl ketone, are geometrically similar. It is possible, therefore, to draw one general curve from which the molecular extinctions at any wave-length may be found for any ketone, excepting the two just mentioned.

The following table gives the wave-lengths and molecular extinctions for the ketones of the general formula CH₃—CO—CH₂—CH₂—R:—

Molecular extinction.	Wave-lengths.	Molecular extinction.	Wave-lengths.
	2000 2410		nore ease
0 -	8220 2416	15	2978 2605
7	8080 2471	17	2949 2631
9	8050 2 510	. 19	29 2 0 2 66 0
11	8024 2544	21	2844 2686
18	2996 2576][]	\/
		21 · 2	2790

Table II.

The maximum molecular extinction for all these ketones at the centre of the absorption band is therefore 21.2. These values are plotted on a curve in fig. 2, the figures on the curve being the last two significant

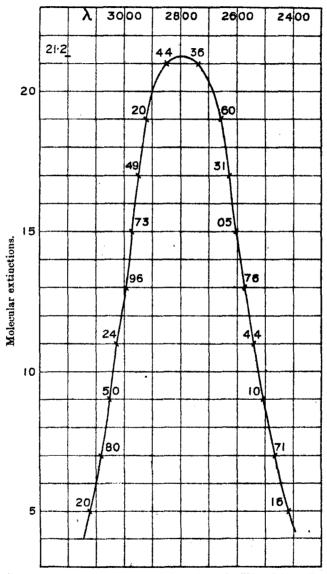


Fig. 2.—Curves for the ketones of the general formula CH3—CO—CH2—CH2—CH2—R.

figures of the wave-lengths corresponding to the extinction shown on the ordinates. Owing to the geometric similarity, the molecular extinction curve of any ketone in the right-hand column in Table I may be drawn by adding

the difference between the centre of its absorption band and 2790 to the wave-lengths in Table II. It may be mentioned here that in the case of ketones with very long side chains the absorption of the alkyl radicals will be superimposed on the normal curve, but with all the ketones examined the absorption of the side chains was found to be practically negligible at wavelengths greater than 2300.

Two important facts may be mentioned in connection with the results of these observations. In the first place, the measurements of the magnetic rotation carried out by Sir W. H. Perkin should bear some relation to the absorption observations, since there is no doubt that the electromagnetic force field theory also can offer an explanation of the magnetic rotation phenomena. A comparison of Perkin's results with the ketones, and those recorded above, certainly shows considerable analogy. For example, Perkin showed that in any one homologous series of compounds it is possible to lay down certain definite laws as regards the relation between magnetic rotation and constitution. Thus he found that the substitution of hydrogen atoms by methyl groups gave rise to a constant change in the molecular rotation, provided that the substitution did not take place in close proximity to a group possessing strongly marked residual affinity. As a result of this he was able to calculate the "series constant" of any homologous series, and in the case of ketones of high molecular weight perfectly accurate values were obtained.

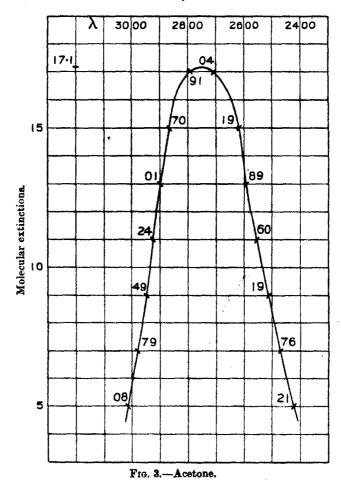
On the other hand, considerable divergences showed themselves in the case of the ketones of low molecular weight. There certainly seems, therefore, some analogy between the light absorption values and those from magnetic rotation if we compare the two divergences together.

Thus the progressive substitution of methyl for hydrogen near the carbonyl group affects the extinction curves, the normal curve not being obtained until the γ -hydrogen atoms are reached.

A still more striking analogy is evidenced when the results with methyl isopropyl ketone and pinacoline are compared. Deviations are observed in the two cases of absorption and rotation. This is especially emphasised in dealing with methyl isopropyl ketone in which the iso group considerably increases the wave-length of the centre of the absorption band. Perkin showed that the presence of this grouping also abnormally increased the magnetic rotation.

A second striking fact is to be found in the chemical reactivity of the ketones, especially of the hydrogen atoms as regards their substitution by halogen atoms. It is well known that the direct substitution of the terminal hydrogen atoms in propane by halogen atoms is slow and difficult to bring

about, whilst in acetone the substitution is carried out with extreme ease. From the absorption results it is obvious that there is a very intimate connection between the carbonyl group and these hydrogen atoms, for substituting them by methyl causes a marked shift in the absorption band. This change is less if a β -hydrogen atom is substituted, and vanishingly small if a γ -hydrogen atom is substituted. In other words, the relation between



the carbonyl group and the α , β , and γ -hydrogen atoms decreases. The reactivity of the hydrogen atoms as evidenced by their direct replacement by halogen, must, therefore, decrease the further they are removed from the carbonyl group, the three γ -hydrogens of methyl propyl ketone being in exactly the same state as the terminal hydrogens of n-pentane.

Attention has already been drawn to the fact that the molecular extinc-

tions of acetone and methyl ethyl ketone are not the same as that of all the other ketones. The extinction curves of these two substances are shown in figs. 3 and 4, from which it can be seen that the molecular extinction of acetone is 17·1, and that of methyl ethyl ketone 19·4. These bodies, there-

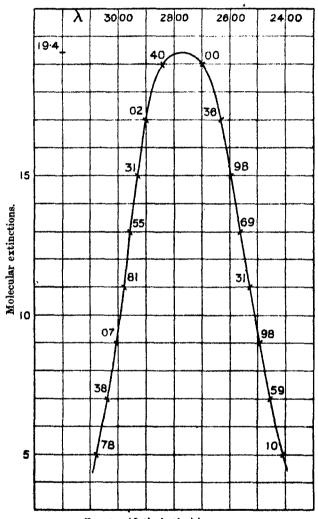


Fig. 4.-Methyl ethyl ketone.

fore, absorb less light than the other ketones, all of which have a molecular extinction of 21.2. This variation seems to be of considerable importance-in view of the fact that acetone is known not to be entirely monomolecular but associated to a certain extent. Ramsay and Shields found the factor of

^{* &#}x27;Trans. Chem. Soc.,' vol. 63, p. 1059 (1893).

association to be 1.26, that is to say, the average molecular weight of acetone is 58×1.26 . Now the association factor x is given by

$$x = \frac{N}{M_a + M_a},$$

where N is the total number of acetone molecules, M, the number of simple molecules, and M_c the number of complex molecules. It is obvious that any association must tend to decrease the absorptive power of the ketone, and it is a reasonable assumption to make that the absorptive power of the associated molecule will be inversely proportional to the number of simple molecules in the complex, that is to say, if two molecules associate, the complex will absorb half as much as the two simple molecules, and so on. Obviously the calculated molecular extinction, in the case of acetone 21·2, will be proportional to N, assuming, of course, that if acetone were unassociated it would behave as a normal ketone in which the maximum molecular extinction is 21·2.

Again, the observed molecular extinction will be proportional to $M_* + M_{\circ}$, for this extinction is the sum of the absorptions of the associated and unassociated molecules for the particular wave-length.

We can, therefore, put the association factor x = Calculated molecular extinction.

In the case of acetone x = 21.2/17.1 = 1.24, which is remarkably close to that actually observed by Ramsay and Shields, namely 1.26.

It would follow from this that not only is it possible to explain the divergency of the absorptive power of acetone from the normal value on the grounds of its association, but also actually to measure the association factor by means of the amount of light absorbed. To calculate the association factor, therefore, the ratio of the two extinctions (calculated and observed) is found. In the case of methyl ethyl ketone the observed value of the molecular extinction is 19.4, while the calculated value is 21.2. The ratio 21.2/19.4 = 1.09 gives the association factor. Unfortunately no values of the surface tension of this ketone seem to have been published from which the value $d \left[\gamma(MV)^{2/3} \right] / dT$ may be calculated, but my results would certainly show that it is associated to this extent.

Summary and Conclusions.

- 1. Fourteen saturated ketones of the aliphatic series have been prepared in a state of optical purity.
- 2. Spectroscopic and chemical tests prove that their purity is above question, and that the absorptive power as determined for these ketones is thoroughly reliable.

- 3. The wave-lengths of the centres of the absorption bands depend on the number of methyl groups in the α and β positions relative to the carbonyl group. Substitution of hydrogen atoms in the γ or further positions has no effect on the absorption band.
- 4. The ketones of the general formula CH₃COCH₂CH₂R have the centre of the absorption band at 2790, and those of the general formula RCH₂CH₂COCH₂CH₂R at 2820, where R is any saturated alkyl radical.
- 5. Substitution of an α -hydrogen atom by methyl causes a movement of the centre of absorption 20 Å.U. to the red for each atom substituted. Substitution for an α -hydrogen atom with formation of the *iso* group causes a shift of 50 units, and when the substitution in the α -position forms a tertiary group the centre of absorption moves 30 units. There is thus an enhanced effect in the case of the *iso* and *tert* groups. The movement of the band caused by the substitution of hydrogen by alkyl is always towards the red end of the spectrum.
- 6. The general results agree markedly with the observations made by Perkin on the magnetic rotation of these compounds. The magnetic rotation is normal for methyl propyl ketone and the higher homologues, but above mal in the case of methyl ethyl ketone, and still more abnormal in the case of acetone. This is shown by the different position of the absorption bands in the case of acetone and methyl ethyl ketone from those of methyl propyl ketone and the higher homologues. A similar agreement between absorption and magnetic rotation is observed in the effect of the iso grouping.
- 7. The results of the absorption measurements agree with the chemical properties of the ketones. The former show that the farther removed from the carbonyl group is a hydrogen atom, the less effect is produced on substitution by methyl, or the less is the relation between the hydrogen atom and the carbonyl group. This is in agreement with the behaviour of the hydrogen atoms on treating the ketones with chlorine or bromine.
- 8. The absorptive power or molecular extinction of all the ketones, with the exception of acetone and methyl ethyl ketone, is 21·2. On the assumption that if acetone were unassociated it would behave normally, the association factor is calculated from its molecular extinction to be 1·24. This number is remarkably close to that found by Ramsay and Shields, namely 1·26.

Similarly, the association factor of methyl ethyl ketone is calculated to be 1.09. The method of light absorption measurement appears to give a means of determining the association factor of a liquid, and also it is not subject to any possible error due to surface concentration phenomena. Ramsay and Shields' work has been criticised on these grounds.

9. The whole of the measurements given are in agreement with the general theory that the absorption band of the ketones is due to the electromagnetic field of the carbonyl group as influenced by the substituents in the immediate neighbourhood.

The author desires to express his sincere thanks to Prof. E. C. C. Baly for much advice and assistance during the course of the research and for facilities for carrying out the work, also to Dr. A. W. Titherley for advice on the purification of the ketones.

Luminous Vapours Distilled from the Arc, with Applications to the Study of Spectrum Series and their Origin.—II.

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(Received October 12, 1914.)

§ 1. Introduction,

This paper is in continuation of a former one.*

It has been observed by Stark, † and subsequently by Matthies; and Child, || that a luminous jet of mercury vapour, distilling away from the are in vacuo, into a region quite remote from the electric field of the arc itself, may be deprived of its luminosity by an independent electric field.

The present paper describes experiments made to elucidate this effect in the case of mercury, and similar observations made upon other metallic vapours.

§ 2. Experiments with Mercury. Electrical Condition in the Luminous Jet.

Fig. 1 shows a form of apparatus suitable for many of the experiments. The mercury cathode is formed by the top of a barometric column, a, connected at the bottom to a rubber tube and reservoir (not shown). The hollow iron tube b, 5 mm. internal diameter and about 1 cm. long, forms the anode. It does not touch the glass walls, but is supported on an iron

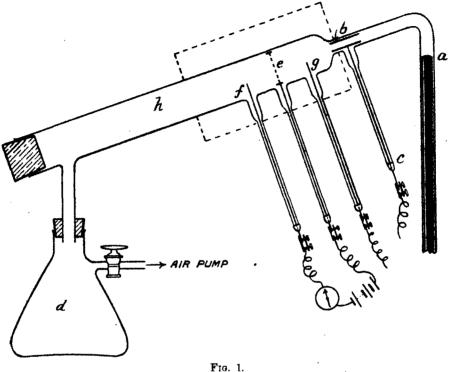
^{* &#}x27;Roy. Soc. Proc.,' A, vol. 90, p. 364 (1914).

^{† &#}x27;Ann. d. Phys.,' vol. 14, p. 530 (1904).

^{‡ &#}x27;Verh. d. Deut. Phys. Gesell.,' vol. 12, p. 754 (1910).

^{| &#}x27;Phil. Mag.,' vol. 26, p. 906 (1913).

wire screwed into it, as shown. The latter passes out through a cemented joint at c.



In using the apparatus the arc was struck by raising the mercury level and allowing a small quantity of mercury to flow over the bend. A current of about 3 amperes was passed. Mercury vapour distilled down the tube h. The upper part of this tube was in an asbestos oven, shown by dotted lines. It was kept hot enough by electric resistance heaters to prevent the mercury from condensing. Further down the mercury was allowed to condense, and fell into the bottle d. A Gaede mercury pump attached to the apparatus was kept going continuously. Under these circumstances the vapour passing from b through c remained luminous until it was condensed.

This general type of apparatus admits of many modifications for different experiments. As shown in fig. 1 the glowing vapour is made to pass through a wire net electrode e, consisting of a few fine iron wires stretched across an iron ring; e forms the cathode of an auxiliary circuit distinct from that of the arc, and used for examining the ionisation of the luminous jet. The

^{*} Ordinary wire gauze obstructs the passage of the vapour too much.

anode of this circuit may be an iron wire at f; a current-measuring instrument and a battery of variable E.M.F. are included in it.

With the arrangements described, the current increases with the E.M.F., at first rapidly then more slowly, but it does not appear to attain a very definite limit. Applying, say, 80 volts* between e and f, the current is of the order of 1 or 2 milliampères.

It is remarkable that the value of the current, though very dependent on the shape and position of the cathode, does not depend at all on the form of the anode, or on where it is placed.

For instance, using e as cathode, we may employ either f, or a wire inserted at g, alternatively, as anode, without affecting the current, although f is upstream of the cathode and g downstream of it, in the rapidly moving mercury vapour. If, on the other hand, we use e as anode, the current will be much larger with g as cathode than with f as cathode. A great variety of experiments with different shaped electrodes, which it would be tedious to describe in detail, have always shown that—

- (1) With two alternative cathodes of the same shape, a larger current passes when the cathode farther upstream is used.
- (2) With a given cathode, the value of the current at any given E.M.F. is independent of the position of the anode.

Experiments made with a testing electrode, or "sound," movable between e and f, and connected to an electrometer, have shown that the fall of potential is almost all in the immediate neighbourhood of the cathode.

It will be observed that the properties of the glowing vapour, regarded as a conductor, are not unlike those of a flame, which is characterised by the great mobility of the negative ions compared with the positive.

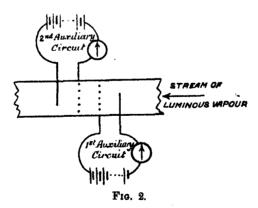
We may, I think, interpret the observed facts as follows:—A certain

* If it is attempted to increase the E.M.F. between the auxiliary electrodes very much beyond this, a discharge is set up, giving rise to new luminosity between e and f. This new luminosity is much bluer in colour than that which comes down from the arc in the absence of any E.M.F. If the anode is upstream of the cathode, so that the negative ions moving from cathode to anode have to make their way against the moving stream of mercury vapour, then discharge starts suddenly and capriciously with the passage of a large current. In the opposite case (anode downstream), as the E.M.F. is increased, a patch of blue light begins to appear on the anode and gradually extends towards the cathode. Its appearance is not accompanied by any sudden rise in the current. We may account for this by supposing that the negative ions approaching the anode produce new ions, with luminosity; but that the new positive ions thus produced are unable to make their way upstream against the general movement of the vapour. Thus they are unable to contribute to the current, and have to recombine with the negative ions from which they were originally separated.

When the anode is upstream the case is different, for the negative ions, of great mobility have no difficulty in making their way upstream.

number of positive and negative ions are carried away from the arc by the stream of vapour. Since electricity cannot accumulate indefinitely on the insulated auxiliary circuit, it follows that when a steady state has been reached the number of positive ions carried down from the arc must be equal to the number of negative, at least if we suppose that each ion is monovalent. Some of the positive ions will be removed at the cathode, others will recombine with negative ions. Owing to the much greater mobility of the negative ions the current passing round the circuit essentially depends on the circumstances at the cathode. The number of negative ions removed at the anode cannot exceed the number of positive ones removed at the cathode, however favourably the anode may be presented to the stream of ionised vapour.

Consider the case when the anode is upstream. Since the electric field is only strong uear the cathode, the current is not even approximately saturated. By this I mean that extensive recombination is going on in the space between the electrodes. On the other hand, after the moving stream of vapour has carried the positive ions into the strong electric field near the cathode, they are all, or nearly all, removed. This view has been confirmed experimentally by arranging a second pair of electrodes with battery and galvanometer, forming a second auxiliary circuit beyond the gauze cathode. The current in this second auxiliary circuit is reduced to a very small fraction of its original value when the first auxiliary circuit is closed with an E.M.F. of 80 volts. The arrangement is indicated diagrammatically in fig. 2.



§ 3. Experiments with Mercury. Effect of Electric Field on Luminosity.

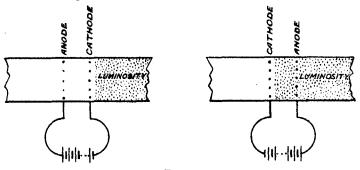
So far we have considered the electrical effects when the auxiliary circuit is closed. Let us now consider the effect on the luminosity of the vapour.

It may be summed up thus: the luminosity is not affected when the

stream of vapour passes the anode, but it is wholly or partially quenched when it passes near the cathode.

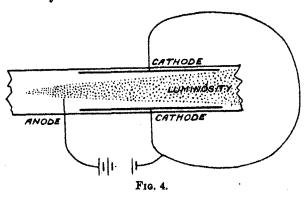
The precise effect depends on the particular shape and disposition of the cathode. Using two wire nets at right angles to the stream, with the upstream net as anode, the luminosity passes the anode and extends to within 1 or 2 mm. of the downstream (cathodic) net, at which point it is permanently extinguished. There is, in fact, a small dark space over the cathode, reminiscent of that observed over the cathode of a vacuum discharge, but not, of course, to be in any way identified with it.

If the upstream net is cathode, the extinction occurs a millimetre or two on the upstream side of it as before, and the whole space between the electrodes is dark (fig. 3).



F10. 3.

Another form of cathode that may be mentioned is a flat plate, several centimetres long, placed parallel to the stream. There is a wedge-shaped dark space over this plate, with its thin end upstream. A cathode consisting of two plates opposite one another, with a metallic connection outside, shows this effect still better (fig. 4). Inside a tubular cathode the luminous stream tapers down similarly.



It has been emphasised that the current passed in the auxiliary circuit depends on the position and shape of the cathode, but is independent of the position of the anode. Exactly the same applies to the extinction effects. For instance, the stream loses its luminosity in passing through a cathode net whether the anode is upstream or downstream of it.

In the absence of any E.M.F. there is always a considerable loss of light as the stream passes through a net electrode. I have not obtained any distinct evidence as to the cause of this, but the greater luminosity of the stream in front of the obstacle may be simply due to its greater density.

An experiment was arranged in which the luminous stream was symmetrically divided into two, one half of it passing through a glass tube 8 mm. diameter and 3 cm. long, and the other half through an iron tube of exactly the same size. The emerging streams were greatly enfeebled by passing through these comparatively narrow tubes, but the stream from the iron tube was not feebler than the other. Thus there seems no special reason for attributing the enfeeblement to contact of the luminous vapour with a conductor.

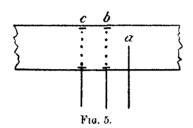
§ 4. Interpretation of the Phenomena. Long Life of the Luminous Centres in the Jet.

The fact that the luminosity can be at once quenched by removing the positive carriers is consistent with two alternatives. Either (1) the luminous centres are charged, and continue to emit in the charged condition, while they are carried a considerable distance from the arc with the stream of moving vapour; or (2) the actual emission only lasts a very short time, the apparent removal of the luminous centres being really the removal of the positive ions which emit a momentary luminosity during neutralisation. What is removed, on this view, is the raw material from which luminous centres would otherwise be formed.

On the second view, the luminous intensity at any point would be proportional to the rate of recombination there. It would therefore, other things equal, be proportional to the product of the concentrations of the positive and negative ions. This is very difficult to reconcile with an experimental fact that has been mentioned above, namely, that no diminution of luminosity is observed at the anode, when this is the first electrode reached by the luminous stream. Negative ions are, without doubt, removed at the anode, and the concentration of those that remain must be diminished. On the theory (2) the luminosity should be diminished proportionately, and if this theory is to stand at all, we must suppose that the negative ions removed at the anode are an insignificant fraction of the whole number that pass.

The following experiment seems to show that this supposition is not admissible.

Two wire nets, b and c, fig. 5, were arranged across the stream of vapour. Using the first one b as cathode, and the wire a as anode, the current was 2.7 milliampères. As already explained, the removal of positive ions



by b was practically complete. Thus the current is a measure of the number of ions that reach this point. Next, using c as cathode and b as anode, the current was found to be diminished to 1.3 milliampère.

It follows, then, that in the absence of a field, the number of positive ions and consequently also the number of negative ones

reaching c is about half the number that reach b, the remainder recombining between b and c. If, then, we make c cathode and b anode, we take out as many negative ions at b as we take out positive at c. In other words, under the particular conditions of this experiment, we take out half the entire number of negative ions that reach b, and we reduce by half the rate of recombination at this point. Yet the luminous intensity is not at all affected. It does not appear, therefore, that the luminosity can be attributed to recombination.

We must, then, fall back on the alternative supposition (1), that the luminous centres manufactured in the arc continue to emit light while the vapour travels a considerable distance. We have to suppose that they are charged positively throughout* to account for their removal by passing near a negative electrode.

It is known, from the kinetic theory of gases, that the velocity of the stream of luminous vapour cannot exceed the molecular velocity. Taking, say, 273° as the temperature of the lamp, the molecular velocity of mercury is about 5×10^4 cm. per second. The mercury glow has been observed to travel 50 cm., and might doubtless be made to travel much further. The time for which mercury remains luminous must therefore be at least one thousandth of a second.

Previous writers have considered it impossible that a molecule once set vibrating could remain vibrating so long, and have therefore been driven back on the alternative view that the luminosity is due to the recombination of ions.

^{*} In the case of mercury. We shall see later that in certain other cases there is reason to regard the luminous centres as uncharged.

A calculation by Lorentz* has been cited, which shows that a single electron performing simple harmonic oscillations of wave-length 6×10^{-6} cm. would lose amplitude in the ratio e:1 in 4×10^{-8} seconds, and could not therefore travel any appreciable distance before extinction.

But have we adequate reason for considering that the vibrating system is of this character? Even on the older views, it is well known that a system of a few electrons equally spaced round a ring, and revolving uniformly, part with their energy beyond measure less quickly than a single one; and more recent speculations of Bohr and others, which rest on Planck's conceptions, question whether the mechanism of light vibrations is of this kind at all. It is sometimes suggested that the observed limit of interference shows that the number of vibrations a molecule can execute is limited to a few millions. But another cause, the Döppler effect of the moving molecules, sets a limit to interference.

Bohr's theory of spectrum series, which has excited so much interest, and which has been so successful in its numerical application to certain spectroscopic data, contemplates the sudden jump of an atom (which may or may not be charged) from one state to another with emission of radiation, does not, so far as at present developed, profess to give any account of when, or why, the jump occurs, and cannot therefore set any limit to how long the emission might "hang fire" after the atom has left the place of excitation.

Upon the whole, therefore, it does not seem that we have any very strong grounds at present for calculating how long after excitation an atom may emit light. If not, we cannot decide, upon these grounds, what view is to be taken of the luminous mercury stream. The evidence which has been thought to exclude the theory of recombination as the cause of luminosity has been given above.

§ 5. Experiments with Various Metals. Some Lines in a Spectrum More Sensitive to Extinction than others. Band Spectra.

The above experiments made with mercury vapour have been extended to other metals, using the methods described in 'Proc. Roy. Soc.,' A, vol. 90, p. 364, 1914. The general results are similar, but the extension has revealed some new and interesting effects not to be observed with mercury.

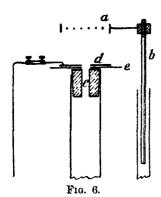
The apparatus requires some additions for observing the extinction effects when the glow passes through a negatively electrified wire net. The net a

^{* &#}x27;Theory of Electrons,' p. 259 (1909).

[†] J. J. Thomson, 'Phil. Mag.,' 1903, p. 681.

[‡] Loc. oit., p. 365.

(fig. 6) is mounted on a metal rod b passing through a barometric column which admits of its being brought to any desired distance above the jet



from which the vapour issues, or being turned out of the way if desired. The anode of the auxiliary circuit may be simply the perforated anode c of the lamp itself from which the luminous vapour issues; or it may be an iron plate d with a hole corresponding to that in c, and insulated from it by the mica washer e. The metal support and contact of d is brought out through the airpump plate which forms the base of the apparatus with an insulating rubber stopper. The barometric column carrying a is brought out in the same way. The apparatus is covered with a

highly exhausted bell-jar as before.

In every case examined the line spectra of metals have been observed to be extinguished by passing through the negatively electrified net. The list is as follows:—Sodium, potassium, calcium, magnesium, mercury, zinc, cadmium, thallium.

The point of chief interest brought out by these experiments is in certain spectra the lines of one series are more easily extinguished than those of another. It is not easy to observe anything of this kind in the case of mercury. But in two cases—sodium and magnesium—it is very conspicuous, and indeed could scarcely escape the attention of anyone making the experiment.

The conditions must not be such as to produce a complete extinction of the whole luminosity, but partial extinction is much more easily achieved than complete extinction, for the latter requires an adjustment of the density of the stream of vapour, dimensions and position of the negatively electrified net, potential applied, etc., which is not in practice nearly so easy to maintain with the metals now under consideration as with mercury.

With sodium, then, if the issuing jet is watched with the spectroscope, it is noticed that on making the auxiliary circuit the D line is far less extinguished than the lines of either of the subordinate series. Several lines of each of these latter series are very conspicuous in the spectrum,

* The difficulty, mentioned in the first paper, of getting a good jet with calcium has been satisfactorily overcome by using, instead of the quartz tube, a tube of quicklime, on which, of course, calcium has no chemical action. The tubes used were drilled out of fine grained marble, and burnt to quicklime afterwards. Only some samples of marble give a coherent quicklime. I believe that fine grain is the essential, but possibly the presence or absence of calcium sulphate, or other impurity, may be important.

and so far as could be observed they all suffered about the same relative diminution of brightness. The small, or in some cases even imperceptible, effect on the D lines was in marked contrast with this. Indeed the difference could be well seen even without the spectroscope, for the greenish luminous jet above the gauze became perceptibly yellower when the key making the auxiliary circuit was depressed.

With magnesium the comparatively faint lines 5712 and 5529 were observed to be very easily extinguished. Next came the blue flame line 4571. The triplet group known as "b" (5183), belonging to the subordinate series, was much less affected by the field than any of these.

In some cases the band spectrum of "magnesium hydride" was seen almost as strongly as the line spectrum. This spectrum is more easily extinguished by the field than the triplet b. The latter is seen on a background consisting of the bright green band of magnesium hydride. In some experiments this background was most strikingly cleared away from b when the circuit was made, leaving the latter almost unaffected.

All these phenomena have at times been seen most strikingly. I must admit, however, that the exact conditions under which they are best brought out are still somewhat obscure. Sometimes it is difficult to get conspicuous extinction effects with any of the magnesium lines, and the appearance or non-appearance of the magnesium hydride bands cannot yet be controlled. The elucidation of these points will no doubt follow with further improvements in technique, which will make prolonged observation easier and diminish the expenditure of time in cleaning, repairing, and recharging the apparatus.

In the zinc spectrum it has been observed that the blue triplet (5182, 4811, 4722) of the subordinate series is distinctly more difficult to quench than the lines 6363, 5310, and 4630. Of these latter, the red line 6363 is much the strongest, and without the spectroscope it can be seen that the light becomes bluer on making the auxiliary circuit, owing to relatively great diminution of the red line.

Similar experiments with cadmium did not show any unmistakable difference in the extinction of the various lines, though it was suspected that the series triplet (5095, 4808, 4682) was less extinguished than other lines.

In the case of mercury, which, to get comparable conditions, was tried in the same apparatus as zinc and cadmium, no indication of any difference between the lines was observed.

Two metals, arsenic and antimony, give luminous jets showing band spectra. The bands are evenly spaced over a considerable region of the spectrum, like

the blue and violet bands of an ordinary nitrogen vacuum tube. After many attempts, I have failed to observe any extinction of these spectra when the auxiliary circuit is made. It would be unwise to build too much on the negative result, for I have occasionally encountered experimental conditions under which the magnesium lines, for instance, were not much extinguished, without understanding clearly what was essential in these conditions. Upon the whole, however, I have very little doubt that the arsenic and autimony spectra are essentially incapable of extinction in this way. Thus, it is natural to assume that the carriers of these particular band spectra are electrically uncharged.

The results obtained in this part of the field are, no doubt, scanty, in comparison with what remains to be done, but they represent a considerable amount of labour, and seem to justify the conclusion that the luminous centres of the principal series in the alkalies are not the same as the luminous centres of the subordinate series. This conclusion is independent of whether we assume, in accordance with the conclusions which have been drawn above, that the centres are excited in the arc, or whether we suppose them to be excited by subsequent neutralisation.

The failure to obtain extinction with the band spectra of arsenic and antimony indicates that no charged particles are concerned in the production of these spectra, and consequently that in these cases, at any rate, the luminosity of the distilled jet cannot be attributed to recombination of ions, and must be excited in the arc itself.

The luminous jets of arsenic and antimony bear so strong a general resemblance to those of the other metals that we cannot reasonably refuse to extend the same conclusion to the latter. This line of argument against the recombination theory of luminosity is independent of that already given, and may be considered confirmatory.

§ 6. Summary.

(1) The conducting properties of a luminous jet of mercury vapour distilled from the arc in vacuo have been examined. The current depends on the shape and position of the cathode introduced into the jet, and is independent of the position of the anode. In the case where the anode is reached first by the stream of vapour, and a net electrode is used as cathode, all the positive ions may be taken out of the vapour that passes through the cathode. There is saturation of the current in the layer near the cathode. On the other hand, recombination proceeds in the rest of the space between cathode and anode, for the electric force is concentrated near the cathode, and near the anode is not strong enough to take out all the negative ions.

- (2) The luminosity of the jet is unaffected by the removal of negative ions at the anode, but is quenched by removal of positive ions at the cathode. Although the removal of negative ions in the former case is not complete, it is considerable enough to show conclusively that the luminosity is independent of the number of negative ions present. Thus the luminosity is not due to recombination of ions. It seems necessary to assume that the luminous centres in the jet are survivors of those generated in the arc itself, in spite of the appreciable time (1/1000 second) necessary for the vapour to travel down the tube. We must suppose these centres to be positively charged to account for their removal at the cathode.
- (3) Experimenting with other metals as well as mercury, it is found that the various lines of a spectrum are not, in all cases, equally extinguished when the jet of luminous vapour passes through a negatively electrified net. Thus the lines of the subordinate series of the sodium spectrum apparently all lose intensity in the same ratio; but the D line of the principal series is much less affected. Thus it is inferred that the luminous centres emitting the principal series are not the same as the luminous centres emitting the subordinate series. Analogous differences have been observed in the line spectra of magnesium and zinc.
- (4) The jets formed by arsenic and antimony, which show band spectra consisting of large numbers of uniformly spaced bands, are not quenched by passing through a negatively electrified net. The luminous centres appear therefore to be uncharged in these cases. With the band spectrum of magnesium hydride it is otherwise.

An Additional Note on the Production of High Permeability in Iron.

By Ernest Wilson, Professor of Electrical Engineering, King's College, University of London.

(Communicated by Dr. J. A. Fleming, F.R.S. Received October 24, 1914.)

The observations recorded in this paper may be regarded as an Appendix to a former paper,* elucidating a point which remained unsettled. It has been shown that if stalloy in laminated ring form is subjected to a magnetising force due to a direct current, and ranging from 3 to 14 C.G.S. units, whilst it is cooling through the temperature at which it regains its magnetic properties, and is at the same time shielded from the influence of the earth's magnetism, the permeability recovered at atmospheric temperature has a maximum value of over 10,000 when the magnetic induction is of the order 6000-7000 C.G.S. units.

It had been shown previously† that high values of the permeability can be obtained without the use of a special magnetic shield, when the iron has impressed upon it a magnetising force due to an alternating current, during the time that it cools through the temperature at which it regains magnetic properties. The authors of this last mentioned paper, however, used an iron tube to inclose the specimen, and the tube itself was heated with the specimen. It seemed, therefore, desirable to discover whether these high values of the permeability can be obtained when there is no question of magnetic shielding.

In a preliminary experiment a small stalloy ring, built up of stampings 0.042 cm. thick, was placed in a small cast-iron box and heated in a gas furnace to the neighbourhood of 800° C. It was subjected to a magnetising force of 13 C.G.S. units, due to a direct current, and allowed to cool to atmospheric temperature during application of the force. When cold, it gave a result in practical agreement with that obtained when stalloy is allowed to cool in a special shield; that is to say, the permeability had a maximum value of over 10,000 when the magnetic induction was of the order 6000-7000 C.G.S. units.

A fresh stalloy ring, built up of stampings 0.042 cm. thick, was then placed inside a small fire-clay crucible. It was allowed to cool as before from about

^{* &#}x27;Roy. Soc. Proc.,' A, vol. 90, p. 343 (1914).

t "The Annealing of Steel in an Alternating Magnetic Field," by H. Pender and R. L. Jones, 'Physical Review,' Second Series, vol. 1, No. 4, April, 1913.

800° C., when subjected to a magnetising force of 13 C.G.S. units, and a maximum permeability of over 10,000 was again obtained.

The conclusion is that it is not necessary specially to shield iron from the influence of the earth's magnetism in order to obtain high maximum permeability by the method of allowing it to cool through the temperature at which it regains magnetic properties, when it is subjected to a magnetising force ranging from 3 to 14 C.G.S. units due to a direct current.

Further experiments have been made with stalloy in the form of straight strips 8 cm. long, 1.5 cm. wide, and 0.053 cm. thick. Eight such strips were taken together to make up a test piece, which was wound with 43 turns of asbestos covered copper wire. The specimen was placed inside an iron tube, which was sealed at each end with an iron cap, the ends of the specimen touching the caps. The whole was then raised to a temperature of about 800° C., and allowed to cool inside a magnetic shield during the application of a direct current of 8.5 amperes in the magnetising coil. When cold, the specimen was removed from the iron tube and tested for permeability. The improvement was small, and had apparently disappeared when re-tested by the makers at their works.

The author wishes to thank Sir R. A. Hadfield, F.R.S., and Messrs. Sankey and Sons for having furnished material for the purposes of these experiments.

Address of the President, Sir William Crookes, O.M., at the Anniversary Meeting on November 30, 1914.

Since the last Anniversary the Royal Society has lost by death sixteen Fellows and six Foreign Members. It is my sad duty to express our united sorrow at the loss.

Sir David Gill—the greatest practical astronomer of our times and a scientific worker of peculiarly high ideals—died in London early in the present year after long illness. Sir David Gill's work as Her Majesty's Astronomer at the Cape of Good Hope brought him great distinction. His energy was superabundant and his enthusiasm unbounded. Owing to his efforts the Observatory at the Cape has become one of the leading observatories of the world. He attracted a keen band of workers, who were encouraged to publish the results of much valuable work achieved under his guidance. He also inspired many younger astronomers, some of whom have now come to the front. His keen appreciation of accurate work, his engineering skill which enabled him to eliminate small systematic errors, made his parallax work with the heliometer the high-water mark of practical astronomy. His work was also directed to great astronomical problems, which he attacked with enthusiasm and persistency. The geodetic work which he directed ranks with the great Russian and Indian works. His 'History and Description of the Royal Observatory, Cape of Good Hope,' contains a remarkable record of his wonderful powers of organisation, his extraordinary determination in overcoming difficulties, and his selfconfidence—fully justified by the outcome of his projects. His best known researches were on stellar and solar parallax, and on the determination of the mass of the moon, and of Jupiter. Gill's single-mindedness and strong personality won him many friends and admirers, who sincerely mourn his death.

The death of Prof. John Henry Poynting has deprived the scientific world of a physicist to whose work it is difficult to do justice in a brief report. Appointed Professor of Physics in Birmingham in 1880, Poynting became a Fellow of the Royal Society in 1888. In 1905 he was elected President of the Physical Society, and was awarded a Royal Medal by the Royal Society for his researches in physical science, especially in connection with the gravitation constant and the theories of electrodynamics, and radiation. His determination of the Newtonian constant of gravitation by the process known as "weighing the earth" was published in 1891. The theorem, known by his name, connecting mechanical motion with electric

and magnetic forces is a fundamental generalisation—and his work, both theoretical and experimental, upon radiation pressure was hardly less important. He proved that a beam of light behaves in all respects like a stream of momentum, and he evolved a method of determining the absolute temperature of the sun, the planets, and of space. He was the author of a well known series of text-books of physics, written in collaboration with Sir J. J. Thomson; he also wrote some interesting popular books on scientific subjects. His position as Dean of the Faculty of Science at the University of Birmingham brought him into intimate contact with many students who will inevitably remember his name with veneration and affection. In Prof. Poynting we have lost a man of delightful personality and remarkable originality.

Prof. George M. Minchin, who died in March, was a man of great versatility, who won renown in more than one branch of natural knowledge. many years he was Professor of Mathematics at Cooper's Hill Engineering College—and he was the author of original and widely used works on Statics, Kinematics, and Hydrostatics. He was a polished writer both of prose and verse, and was the master of a clear and graphic style. His pioneer experimental work on photo-electricity and selenium cells was begun in 1877. when he discovered that electric currents are produced by the action of light upon silver plates coated with emulsions of bromide or other silver salt; the cells he called "impulsion cells," which had their sensitiveness to light altered by slight impulses or taps, embodied the principle of the coherer used for the reception of the Hertzian waves. He afterwards observed that similar results could be obtained by using two selenium-coated aluminium wires dipped in certain solutions; and in 1908 he described, in a communication to the Royal Society, further researches on new forms of the photo-electric cells, and on "seleno-aluminium bridges," which consisted of two aluminium plates separated by a thin flake of mica, and having a layer of sensitive selenium across one end of the mica and the adjacent portions of the aluminium plates. He used his cells to obtain measurable electromotive forces from the light of stars, and thus determined the relative intensity of the light of some of the fixed stars and planets. The results of his investigations agreed closely with those of photometric measurements of stellar magnitude. When Cooper's Hill College was closed Prof. Minchin went to live at Oxford, where he remained until his death. He was elected a Fellow of the Royal Society in 1895.

The death of Sir Joseph Wilson Swan in his 86th year has deprived the scientific world of a distinguished investigator—and me, personally, of an intimate and valued friend. Sir Joseph Swan had a mind of extraordinary

fertility of invention. At the same time he was endowed with an unusual amount of business capacity—a fortunate combination of qualities rarely found.

In his young days he was specially interested in photographic research. He was the discoverer of the first commercially practicable process of carbon printing, which he patented in 1862. He discovered the method of making extremely rapid dry plates, which revolutionised photography; and he also invented and patented the bromide printing process. Another field of research in which he won renown was the application of electricity in illumination. As early as 1860 he had constructed an electric carbon filament glow-lamp, which he subsequently improved, finally arriving at the form which, until quite recently, was universally used. He discovered a valuable method of rapid deposition of copper, and also devised improvements in the construction of secondary batteries. His distinguished services to Science were recognised by the Royal Society, which elected him to its Fellowship in 1894, and 10 years later awarded him the Hughes Medal, by the Society of Chemical Industry, which bestowed upon him a gold medal, and by the Royal Society of Arts, which awarded him the Albert Medal in 1904. By his discoveries and inventions Sir Joseph Swan did much to benefit what we perhaps mistakenly call "civilisation"; the practical value of his investigations, more particularly in the applications of electricity, is unequalled in the history of Science.

Dr. George James Burch, who had been elected a Fellow of the Royal Society in 1900, passed away in March this year. Dr. Burch for many years was Professor of Physics at University College, Reading; he was also a University Extension Staff Lecturer at Oxford-where he lived. His early investigations were connected with electro-physiology, and he discovered a method of analysing electrometer curves, a description of which he published in 1890. His later years were devoted to the study of the physiology of vision; he published an interesting memorandum on Sight Tests, as well as a book describing the practical work done under his direction at the Physiological Laboratory at Oxford. In this book the highly original tests and exercises he evolved were described. His knowledge of visual physiology was unique, and he achieved an eminent degree of success in the subject which he made specially his own. In his keen prosecution of research he was unsparing of strength and energy; it is said that in order to study colour-blindness he made himself temporarily colour-blind by exposing his eyes to the sunlight in the focus of a burning glass behind different coloured glasses.

In February the death occurred of Horace Bolingbroke Woodward, who,

from 1867 to 1908, had taken an active part in the Geological Survey. He was in charge of the work in England and Wales for the last seven and a-half years. Woodward's knowledge of British geology, and especially of stratigraphical geology, was profound. He published many memoirs on geological subjects, and he was the author of a valuable and original work on the Geology of England and Wales. He became a Fellow of the Royal Society in 1896, and served on the Council of the Geological Society for several years, being Vice-President from 1904 to 1906. He was an indefatigable worker and his writings were characterised by the great stress he laid upon accuracy in the minutest detail. He also had a gift for writing in an interesting and non-technical style which made a special appeal to the general reader. Although he was forced to retire from the Geological Survey some time before his death, he continued his literary work as long as strength would allow—and almost to the very end of his life he was engaged in preparing the statistical part of a Survey Memoir on Water Supply. His many friends, and especially those who were associated with him on the Survey, will long remember him with grateful affection for the help and sympathy he willingly lavished, and for the example he set of untiring industry and enthusiasm.

Dr: Albert C. L. G. GUNTHER had a distinguished career as a zoologist, and the progress of the science owed much to his investigations. He was appointed Keeper of the Department of Zoology of the British Museum in 1857—under his charge the department was brought to a high state of efficiency. He published many communications in the 'Philosophical Transactions' and the 'Proceedings' of the Zoological and Linnean Societies, and he founded the 'Record of Zoological Literature,' editing the first six volumes. In 1878 he received a Royal Medal from the Royal Society for his work in zoology and especially for his researches in herpetology and ichthyology.

The death of Dr. Walter Holbrook Gaskell in the full tide of his powers is a heavy blow to his friends and a great loss to the scientific world. Dr. Gaskell exercised a powerful influence upon the development of physiological science. His early research work in physiology was inspired by Michael Foster and by Karl Ludwig of Leipzig. His work upon the mechanism of the beat of the heart was that of a pioneer of great originality and intrepidity. His investigations of the sympathetic nervous system were of fundamental importance, and his generalisations were far-reaching and based upon keen observational powers. His views upon morphological questions were original and in some respects at variance with those of other authorities. His later years were spent in accumulating material in support

of his theories and in expounding them in fuller detail. He was a keen and vigorous worker in physiology. He can ill be spared and his loss will long be severely felt.

The death of Dr. Philip Henry Pye-Smith after a long and busy life occurred in May. Owing to ill-health he passed the latter years of his life in retirement. He will be greatly missed by the wide circle of friends and acquaintances who were attracted by his geniality and kindness, his wide interests and profound knowledge. He led a life of great public activity, and received many honours from Scientific Societies and Universities. He served on the Council of the Royal Society in 1891–92; besides his work as physician to Guy's Hospital, he found time to edit Fagge's work on the 'Principles and Practice of Medicine.' He also published many papers on medical subjects. He was one of the great authorities upon skin diseases, and was keenly interested in the history of Medicine. He was an admirable lecturer; countless students have reason to be grateful to him for his careful training and his insistence upon the importance of accurate observation and cautious deduction.

Geological science suffered a severe loss in the death, in August, of ALFRED JOHN JUKES-BROWNE. At the end of a successful University career at Cambridge, where he did excellent work under Prof. T. G. Bonney, JUKES-BROWNE joined the Geological Survey. Afterwards he specialised in the palæontological zones in English chalk strata. He also investigated the oceanic deposits of Barbados, and he was the author of highly successful and widely used text-books on general Geology. He received the Murchison Medal of the Geological Society in recognition of his valuable services. Although severely hampered throughout the greater part of his life by ill-health, and for the last twelve years forced to live a secluded and quiet life, his work will long survive, and his name be remembered as that of one of the most distinguished geologists of his day.

In the Right Hon. JOSEPH CHAMBERLAIN and VISCOUNT CROSS the Royal Society has lost two distinguished members. They put forth no claim to be regarded as scientific specialists, but each was inspired to turn some page of "Nature's infinite Book of Secreey."

The narrative of the career of Sir John Murray, who also died this year, is full of interest and romance. Owing to his tireless activity and his strong individuality, he was responsible for an amount of brilliant work hardly equalled by that of any other investigator in the same sphere. His early scientific training, during which he refrained from specialising in any particular branch, but studied all subjects which interested him, laid the foundation of his extraordinarily wide knowledge. His adaptability and

resource were qualities which were invaluable to his colleagues upon the "Challenger" Expedition, to which he was appointed Naturalist. He proved himself to be a remarkably acute observer, of strong deductive powers and sound judgment: he had the courage of his convictions and was never chary of attacking established views when he believed he could prove them to be His theory of the origin of Coral islands, which after much controversy was finally almost universally accepted, was from the geological His investigation of the fresh-water lochs of point of view revolutionary. Scotland is a remarkable piece of work. He was keenly interested in the exploration of the Sea, and made many voyages on his own yacht for the purpose of oceanographic investigation. He had a strong business instinct, and although throughout the whole of his long career he was deeply imbued with a love of Research for its own sake, he was always capable of quickly perceiving the commercial applications of his conclusions. Upon several occasions he gave valuable practical advice to the Government.

The late LORD STRATHOONA AND MOUNT ROYAL—elected a Fellow of the Royal Society in 1904—will long be remembered as one who gave his whole life and all his powers to the extension of the British Empire and the strengthening of the bonds of its union. His indomitable courage in the early dangerous and difficult days which he spent in Labrador and on the shores of Hudson's Bay, his foresight and determination in carrying out the project of the Canadian Pacific Railway, admirably revealed the temper of the man. The memory of his splendid patriotism and generosity will live long after him.

In June the death occurred of Joseph Reynolds Great in active worker in physiological and botanical research and a prolific writer on these subjects. He made a special study of enzyme action, and was the discoverer of lipase in the germinating seed of the castor-oil plant. His writings are characterised by great lucidity and accuracy, and his contributions to botanical science are of considerable importance.

Another name must be added to the heavy list of losses sustained by science during the past year—namely, that of ALEXANDER ROSS-CLARKE, in charge of the Trigonometrical Operations of the Ordnance Survey from 1854 to 1881, and whose knowledge of geodesy was unsurpassed by that of any man of our time. His genius for mathematical calculation excites keenest admiration; his treatise on 'Geodesy' is universally admitted to be the best book on the subject.

Among the Foreign Members of the Royal Society whom death has recently removed from our midst are Dr. Weir Mitchell, Prof. L. Hermann, Prof. A. Weismann, Dr. H. Kronecker, Dr. G. W. Hill, and Prof. E. Suess.

Dr. Silas Weir Mitchell died in January last in his eighty-fifth year, his mental and bodily vigour continuing to the end. He was one of the foremost neurologists of the day, and his numerous books on nervous diseases made his name a household word in the profession. Moreover, he achieved a remarkable success in the domain of fiction, some of his novels taking a foremost place.

Prof. LUDIMAR HERMANN, of the University of Königsberg, was the author of the 'Handbuch der Physiologie,' and for many years was Editor of the 'Jahresberichte über der Fortschritte der Physiologie.'

Prof. AUGUST WEISMANN, of the University of Freiburg, received the Darwin Medal of the Royal Society in 1908. He contributed largely to the study of Evolution and was one of the earliest writers in support of the Darwinian theory.

Dr. Kronecker was a tireless worker in physiology. His researches at the Berne Physiological Institute won for him a truly world-wide reputation. He was the author of valuable monographs upon the physiology of the muscles and nerves.

The death of George William Hill removes from our midst one of the leading exponents of nineteenth century Celestial Mechanics. The two papers which contained his chief researches in the Lunar theory have, at the hands of Poincaré, Sir George Darwin, and others, created a new method of treating Lunar problems, and have also led to the formation of a new theory and tables of the Earth's moon. The theories of Jupiter and Saturn, with tables for these planets—which he completed in 1892—have superseded all previous tork. His papers in four volumes are published by the Carnegie Institute of Washington. He possessed unusual intuition—another name for genius—into the possibilities of the subjects he treated, and the originality of his methods was one of their most distinctive features.

Prof. Eduard Suess was a geologist of great eminence, whose position amongst exponents of the science was unique. His monumental work on the 'Face of the Earth' has been aptly described as the culmination and crown of the geology of the nineteenth century. It was Suess who brought together and collated the observations of all who have studied the form of the earth, and in addition much original work in both stratigraphical and paleontological geology was due to him.

Probably at no time in its history has the financial responsibility of the Royal Society been more perplexing than it is to-day. At the last Anniversary Meeting the President, Sir Archibald Geikie, referred to the annual expenditure on the National Physical Laboratory. He pointed out that should

there be any serious falling off in receipts—such as might be caused by an interruption or stagnation of industrial enterprise—there would necessarily be a serious deficit, and that it would be impossible promptly to reduce the working expenses—at that time met by the receipts.

The financial strain foreshadowed by my predecessor has now befallen us. It is, however, to be hoped that, in view of the national character of the Laboratory, of the great services which it is rendering to the nation—services which are of extreme importance at the present crisis,—the Government may see fit to come to our assistance, so as to enable the Society to continue the work of this great Institution—a work which the Society's own resources will not enable it to do in existing circumstances. Those resources must of necessity have a great strain thrown on them in other directions, for we have now to face heavy liabilities in connection with our own 'Catalogue of Scientific Papers (1880-1900)' and the preparation of the 'International Catalogue of the Scientific Literature of the Present Century.' On the foundation of the latter, the Society undertook to be responsible for the completion of the former. The cost of this has, owing to the vast increase of scientific literature at the close of the last century, proved to be largely in excess of the sum provided for its production, mainly by the generosity of the late Dr. Ludwig Mond; and thus the necessary funds have had to be supplied by the Society itself, as at the present time it would be out of the question to appeal for further donations for this object. On the other hand, while it is certain that, owing to the World upheaval, a large part of the subscriptions from Continental nations, by which the cost of the angluction of the International Catalogue is defrayed, will not be forthering, the Society remains liable for the expense of the issue now in course of publication—an expense which must be large.

At the time of our greatest need we are confronted with the possibility of a serious diminution in income. The strengthening of the hands of our Government has rightly been regarded as having the first call on those in a position to render financial aid. Like every private individual the Royal Society must limit its expenditure and practise economy. On the other hand, we have imperative responsibilities and a duty to the nation which cannot be shirked. We dare not allow ourselves to slacken in our devotion to Research—but the fact remains that our need of money is greater now than ever. Our special object is to vivify and stir the spirit of philosophic inquiry and of scientific glory, at a moment when another kind of "Glory" transfixes the whole of the civilised—or shall we say uncivilised—world. I will quote from Sir Humphry Davy's discourse on the occasion of his taking the Chair of the Royal Society for the first time in 1820;—"Let us then

labour together and steadily endeavour to gain what are perhaps the noblest objects of ambition-acquisitions which may be useful to our fellow creatures. Let it not be said that at a period when our Empire was at its highest pitch of greatness, the Sciences began to decline; let us rather hope that posterity will find in the 'Philosophical Transactions' of our own days proofs that we were not unworthy of the times in which we lived." Science ought to be one of the great bouds of union and peace between Nations. Surely it would be a disaster to the whole world if the usefulness of the Royal Society were to be restricted by mere lack of funds. Many enquiries of vast importance have not received the support they deserved from the Royal Society solely owing to want of funds. To-day money is diverted to other urgent uses. It is nothing short of scientific tragedy that learned Societies are for the moment overlooked. It is the duty of those whom Davy spoke of as having been honoured with the rank of Generals in the army of scientific workers, to keep before the eyes of the public the urgent need of money for Science, and the colossal importance of scientific work for the welfare of the nation. We are emphatically the Trustees of the Future.

At a time like the overwhelming present, when our existence is at stake, it behoves those of us who cannot actively share in the great upheaval to take stock of our position among the nations of the civilised world. It is our duty, without morbid regret for the past, or eraven fear of the future, to think of our own aims, and to reflect upon the aims of our adversaries as far as we are able to understand them.

In 1896 the Rumford Medal of the Society was given in duplicate to Prof. Rumforn, and to Dr. Philipp Lenard, Professor of Physics at Heidelberg. Prof. Rentgen is stated by a Berlin paper not to care to retain his Medal and has given it to the Red Cross. Dr. Lenard is credited by a German paper with the following savage outburst:—

"Down, then, with all considerations for England's so-called culture. The central nest and supreme academy for all hypocrisy in the world, which is on the Thames, must be destroyed if the work is to be done thoroughly. No respect for the tembstones of Shakespeare, Newton, and Faraday!"

The recent manifesto of the German Professors is a monstrous utterance, and in the words of a German paper is a grave symptom of national insanity.

Reading between the lines I think we may see that the signatories recognise they have been betrayed by facts, and they are forced to make an appeal to theory. So also we believe they will find their reliance on brute force is doomed to end in failure. On the other hand, we look beyond the "Sacrifice of blood and treasure" to the vindication of an idea, the

establishment of a principle. The dignified reply of the English scholars to the manifesto of the German intellectuals is confined to a recital of facts.

The united universities of France have addressed to the universities of the neutral nations a noble and imposing document in which the claims of Germany are answered in a manner beyond all question.

The Royal Society is always cosmopolitan in spirit, and we should be unworthy of our heritage could we not, even at this desperate moment, take a dispassionate view of events, and preserve a well-balanced and rational attitude towards our contemporaries of German nationality.

Our senior Honorary Secretary, Sir John Bradford, whose absence we greatly regret, has recently gone to the front as consulting physician to the forces. We are glad to congratulate him on filling a position of such vital service, and we wish him success in the strenuous work certain to fall to his lot.

The report of our Council gives a full notice of important events of the past year. But there are some results of investigations to which I call special attention.

The work of Prof. W. H. Bragg and his son, W. L. Bragg, on the application of X-rays to crystal structure form a splendid "first fruits" of an entirely new field of crystallographic research. Mr. H. G. T. Moseley has recently studied photographically the X-ray spectra of many of the elements, and he furnishes some very interesting results relating to the connection between the spectrum and the atomic number of the element.

In the Bakerian Lecture on Series Lines in Spark Spectra, Prof. A. Fowler has a direct bearing on the constitution of the atom—confirming the theoretical work of Dr. Bohr. The peculiarities of the series of new lines produced by passing strong discharges through helium tubes containing hydrogen as an impurity led to the search for other series of similar character, and experiments were performed with magnesium, calcium, etc., in which many new enhanced lines were obtained. It is interesting to notice that Bohr's theoretical formulæ for hydrogen and helium agree closely with the observed facts; if his formulæ are adopted, the mass of the hydrogen atom in terms of the electron is 1836 ± 12 .

The subject of the constitution of the atom has come into extreme prominence—great advances have been made—while much light has been thrown on the ultimate structure of matter. Years ago, during the persistent and systematic fractionation of yttrium, I explained that I had succeeded in separating the atoms of the so-called element into groups; these groups undoubtedly exhibited different phosphorescent spectra and presumably had different atomic weights—although from the chemical point of view all the

groups behaved similarly. I concluded that, of the lines and bands of the compound spectrum of an element, some are furnished by certain atoms and some by others. I pointed out that this was not likely to be an isolated case; that probably in all so-called elements the whole spectrum does not come from all the atoms-that different spectral rays come from different atoms, which may be interpreted to mean that there are definite differences in the internal motions of the several groups of which the atoms of a chemical element consist. I ventured to suggest a possible explanation of these facts, based on the assumption that acting on the original protyle were two forces—one of the character of Time, accompanied by a lowering of temperature, while the other, swinging to and fro like a pendulum, and having periodic cycles of ebb and flow, rest and activity, would be intimately connected with the force of electricity. I arrived at a presentation of the elements on a lemniscate path which seemed to me to throw some light My researches seemed to show that on the question of their genesis. the persistence of the ultimate character, the eternal self-existence, the fortuitous origin of the chemical elements, could no longer be regarded as satisfactory.

Apparently bodies exist which possess close upon the same atomic weights and combine in definite proportions with other substances and yet exhibit certain minute differences. For these substances, which are capable of being isolated and identified, I suggested the name "meta-elements." Thus there appears to me to be a gradation of molecules of different ranks between the atom and the compound—and these aggregations of atoms in certain circumstances might well pass for simple elementary bodies.

In recent years the old idea of the ultimate atom as a solid particle, spherical or otherwise, has slowly, almost imperceptibly, given way to the more rational conception of a minute planetary or "Saturnian" system of dazzling complexity; the conception is many minded, aided here and there by facts that failed to fall in with the old lines of thought. Among the most prominent men through which the new conception has come to light, we have Kelvin, Stoney, Thomson, and, more recently, headed by Sir Ernest Rutherford, a host of vigorous workers in the new science of radio-activity, who have built up a conception of atomic physics often "hard to be understood," but that probably is a move in the right direction. Rutherford supposes the atom to be composed of a nuclear positive charge, exceedingly small compared with the sphere of action of the atom, and consisting of a number of unit charges. Surrounding this nucleus is an external shell in which a number of separate negative electrons are distributed. Prof. Soddy-whose name is closely associated with that of Sir Ernest Rutherford—is one of the earliest workers in radio-activity, and has developed a theory of the chemistry of the radio-elements based upon the periodic law and a modified form of lemniscate spiral where the existence of pseudo elements having slightly different atomic weight but identical chemical properties are set out. These "isotopic" elements occupy the same place in the Periodic Table. He has thus arrived, by a totally different path from the one I travelled, at the conception of an element having atoms of different weight though chemically identical. The theory has recently received some confirmation by the analyses of the lead that is found in the minerals pitch-blende, thorianite, etc. In my own laboratory a spectroscopic examination of the lead from Cornwall pitchblende has shown traces of thallium not found in pure assay lead; the unexpected presence of this element may have some-bearing on the slightly different atomic weight values recorded for the lead extracted from the radio-minerals.

Without risking a charge of being unduly optimistic I think I may believe we are on the brink of striking developments in our knowledge of the structure of the clusive atom. Whatever may be the outcome of researches now prosecuted with so much zeal and success, I feel that Addison was speaking with the voice of prophetic Truth when, more than a hundred years ago, he said: "Every atom is a standing miracle and endowed with such qualities as could not be impressed upon it by a Power and a Wisdom less than infinite."

MEDALS.

With great pleasure I announce that the Copley Medal this year is awarded to Sir Joseph John Thomson, in recognition of the value of his researches in Physical Science. His early work in the investigation of electrical phenomena showed he possessed a high degree of experimental ingenuity and skill: by his study of the passage of electricity through gases he elucidated the nature of the negative electrical particles, thus providing an experimental basis for the atomic theories of the nature of electricity. His treatise on the Conduction of Electricity through Gases won for him a world-wide reputation as a physicist—to which subsequent work has added. To him is due the investigation of the nature of the positive carriers of the electric charge; his method of positive ray analysis puts a new and extraordinarily valuable tool into the hands of investigators. His experimental work has always been controlled and confirmed by theoretical considerations; his work at the Cavendish Laboratory at Cambridge has greatly extended our knowledge of the structure and nature of matter.

The two Royal Medals annually presented by the King have—with His Majesty's approval—been assigned to Prof. E. W. Brown and Prof. W. J. Sollas. Prof. E. W. Brown, who now occupies the Chair of Mathematics at Yale University, devoted himself for many years to the study of the movements of the moon: and by incredible industry seven years ago he brought to a successful conclusion his investigation of this fundamentally important practical problem. He has recently further studied some phenomena which known gravitation causes do not explain, and he has extended his investigations to the General Theory of Orbits. His work in dynamical astronomy has been remarkably fruitful, and doubtless the years to come will add lustre to his already brilliant reputation.

The Royal Medal—awarded to a worker in Biological Science—this year has been conferred on Prof. Sollas, who is a pioneer in many fields, and has made many valuable contributions to our knowledge of geology, mineralogy, zoology, and ethnography. His monograph on Sponges is a classic on the subject. He has perfected a method of obtaining transverse sections of fossil organisms and thus he has obtained a knowledge of the structure of certain specimens which long have been the subject of dispute. We hope that Prof. Sollas will have many opportunities of extending his investigations which already have borne so much valuable fruit.

The recipient of the Davy Medal is Prof. W. J. Pope, who has made highly important discoveries in stereo-chemistry, and whose work has thrown much light upon the relation between chemical constitution and crystalline structure. In collaboration with Profs. Perkin and Wallach Prof. Pope has published the results of many experiments dealing with the isolation and' investigation of optically active compounds of nitrogen, tin, selenium, and sulphur; he explains their activity by supposing that the radicles in the active compound are tetrahedrally arranged round a central atom as in carbon compounds. With Prof. Barlow he has more recently been engaged in the establishment of a theory dealing with the connection between crystalline structure and chemical constitution. He has succeeded in reproducing the crystalline form of most substances of known composition, basing his work upon the assumptions of his theory—the experimental and theoretical results show a remarkable concordance. He has further suggested a theory of "valency volume" which is leading to important developments in the investigation of atomic volumes.

The Rumford Medal is awarded to Lord Rayleigh, in token of the Council's appreciation of the mathematical and physical work associated with his name. Lord Rayleigh has, perhaps, done more than any scientific man living to stimulate research; his work in the sciences of Heat and Radiation

has paved the way for remarkable advances, both theoretical and experimental. The Copley Medal was given to Lord Rayleigh in 1899, but the Council wish to offer him some further mark of their recognition of the great value of the research which he still continues to pursue with such conspicuous success.

The Hughes Medal is this year conferred upon Prof. J. S. Townsend, of the University of Oxford, for his work upon molecular conduction in gases, and upon the nature of the disruptive discharge. Prof. Townsend has made a brilliant investigation of the phenomena of conduction by the ionisation of gases by means of Röntgen and similar radiations. The study of the diffusion of the ions of gases led to very important conclusions about the size and nature of gaseous ions—and the theory of ionisation has been greatly extended by Prof. Townsend's work.

The Darwin Medal this year is awarded to Prof. Poulton, in recognition of the value of his researches upon the curious phenomena of mimicry and protective resemblance in insects. Prof. Poulton has brought together a vast number of facts which confirm Darwin's theory on the subject, and he has recently devised and organised a remarkable series of breeding experiments with species of insects in order further to test his conclusions.

Spectroscopic Investigations in Connection with the Active Modification of Nitrogen. IV.*—A Band Spectrum of Boron Nitride.

By WILFRED JEVONS, A.R.C.Sc., D.I.C., B.Sc.

(Communicated by A. Fowler, F.R.S. Received October 23, 1914.)

[PLATE 2.]

Introductory.

Last autumn Prof. Strutt observed that the vapour of boron trichloride, when admitted into the afterglow of active nitrogen, developed a band spectrum, which he photographed with a quartz spectrograph of small dispersion. It seemed likely that this result might be of interest in view of certain facts already established in connection with compounds of the chemically related elements carbon and silicon, namely, that the interaction of carbon compounds and active nitrogen developed the cyanogen bands,† and that the vapour of silicon tetrachloride in the afterglow gave rise to a band spectrum of silicon nitride.‡ Prof. Strutt, therefore, invited me to continue the boron experiments with a view to tracing the origin of the new system of bands, and determining the numerical relations existing in it.

The remarkable scarcity of boron lines lends additional interest to any new work on the spectroscopy of boron as a possible means of detecting hitherto unrecorded lines, or of eliminating others formerly attributed to boron. In this connection Sir William Crookes§ has shown that the boron lines are only three in number, viz., λ 3451·50, λ 2497·83, λ 2496·89 (Rowland scale), and that some lines# observed by Eder and Valenta and others were due not to boron but to impurities.

The new bands have been attributed to the nitride of boron for reasons which will appear in due course.

Experimental.

In order to render a detailed examination possible, the spectrum was photographed with instruments giving greater dispersion than that employed

^{*} I, A. Fowler and R. J. Strutt, 'Roy. Soc. Proc.,' A, vol. 85, p. 377 (1911); II, A. Fowler and R. J. Strutt, 'Roy. Soc. Proc.,' A, vol. 86, p. 105 (1912); III, W. Jevons, 'Roy. Soc. Proc.,' A, vol. 89, p. 187 (1913).

⁺ II, p. 112.

[‡] III, p. 192.

^{§ &#}x27;Roy. Soc. Proc.,' A, vol. 86, p. 36 (1911).

^{||} Kayser, 'Handbuch der Spectroscopie,' vol. 5, p. 137.

by Prof. Strutt. This, of course, necessitated longer exposures. The arrangement of a pair of aspirator bottles and a muslin bag of chopped phosphorus described by Prof. Strutt* for storing and purifying the nitrogen had been found in previous spectroscopic work to be somewhat inadequate for these long exposures. After the aspirator had been emptied of its pure nitrogen, it was necessary not only to interrupt the exposure for the process of refilling from a commercial nitrogen cylinder, but also to wait some time afterwards for the fresh gas to purify by standing in contact with the phosphorus before resuming the exposure.

In the present work, therefore, Prof. Strutt's holder was duplicated; two pairs of aspirators with bags of phosphorus were arranged on the same carriage, with a single drying tube and a suitable arrangement of glass taps, so that a flow of pure nitrogen could be maintained for any length of time, by using the two halves of the arrangement alternately. In the meantime, the half not in use was shut off and refilled from a cylinder, and ample time was allowed for the purification of the gas. The dual holder thus presents many advantages over the single arrangement for spectroscopic investigations. The remainder of the afterglow apparatus was exactly the same as that previously employed.

The first experiments of the new series were confined to the interaction of boron triebloride and active nitrogen. The trichloride is an exceedingly volatile, colourless liquid, boiling at 18° C., and fuming strongly and decomposing on exposure to the atmosphere. A sample was supplied by Prof. Strutt, and the remainder prepared in the Chemical Department of the Imperial College. It was made by passing chlorine over heated amorphous boron, and collected in a vessel cooled in a freezing mixture and containing mercury (to remove excess of chlorine). The product was finally purified by fractional distillation.

On the introduction of the vapour of the trichloride into active nitrogen, a very pale blue-green glow is produced, the colour being readily distinguishable from the vivid green of the boron flame so well known in chemical analysis. The spectrum of the glow consists of the new system of bands, the three boron lines, and bands of impurities, namely, nitrogen and cyanogen.

The New Bands.

The new bands degrade throughout to the less refrangible side, and are quite distinct from the headless, wavy bands (Plate 2, strip 1) observed by others and tabulated by Kayser under the title of oxide spectrum. † The

^{* &#}x27;Roy. Soc. Proc.,' A, vol. 88, p. 539 (1913).

^{† &#}x27;Handbuch der Spectroscopie,' vol. 5, p. 138.

oxide bands consist of alternate, indefinite maxima and minima occurring at or near λ 639, 620, 603, 580, 545, 518, 493, 471, 452. The new spectrum extends over a very large range, namely, from the red to the region of the shortest wave-lengths conveniently investigated with a quartz spectrograph. A general examination of plates taken with a larger quartz instrument showed the existence of two principal systems of bands. One of them, in the ultra-violet, is a very complex system in which some of the bands appear to have double heads on account of the overlapping of different constituent series (Plate 2, strips 5 and 6). The other, occupying the visible part of the spectrum, is of comparatively simple structure, and consists of prominent bands with double heads (Plate 2, strip 4). As the dispersion of the quartz instrument is comparatively small (25-50 Å.U. per millimetre) in the visible region, for study in further detail this portion of the spectrum was photographed with a Littrow prismatic spectrograph, the dispersion varying from about 8.5 Å.U. per millimetre near λ 4000 to 40 Å.U. per millimetre near λ 6500.

The heads were measured with regard to an iron comparison as far as λ 2330,* beyond which point the copper arc was employed as the comparison spectrum. No measurements have been made of the structure lines of any of the bands.

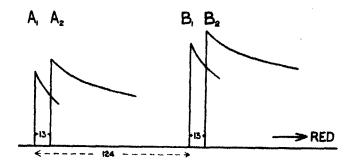
The Less Refrangible System (a).

On the larger dispersion photographs, not only do the less refrangible bands appear double as stated above, but each of the component heads, A and B, is itself a close doublet (Plate 2, strips 2 and 3). Thus a typical band in this region may be said to have four heads, A₁, A₂, B₁, B₂. In the case of A₁ and B₁ the structure lines fall off very rapidly in intensity as their distances from the head increase. A₂ and B₂, on the other hand, have series of structure lines which are easily resolved on the photographs, and persist in intensity for considerable distances from the heads. These features may conveniently be represented diagrammatically, as in the figure, the heights and slopes of the curves indicating roughly the variations of intensities of the lines throughout the band.

From Table I, giving the results of measurement of this system, it appears that, in the first place, the two doublets A_1 - A_2 , B_1 - B_2 of each band have the same interval on the wave-number scale, and this interval is constant throughout the system. The measured intervals vary between 11 and 15, the mean being 13. The discrepancies are attributable to the extreme

^{*} The head of smallest wave-length measurable by Burns' Iron Arc Standards ('Zeitsch. f. Wiss. Photog.,' vol. 12, p. 219 (1913); 'Lick Obs. Bull.,' vol. 8, No.-247 (1913)).

difficulty of measuring a close pair of heads with precision. The difficulty is enormously greater in the case of bands than of lines. Secondly, the



component doublets of a band are also equally separated throughout the system within the limits of error of measurement, the mean separation, A_1 - B_1 , being 124.

Table I.—The Less Refrangible System (a).

λ. Wave- length (I.A.).	Intensity.	n. Wave- number in vacuo.	Designa- tion.	m.	p.	Δn O-C.	Remarks.
68 ^{71 · 2} 65 · 1 63 ^{21 · 8} 15 · 7	6	15691 15706 15815 15829	B ₂ B ₁ A ₂ A ₁	60	74	-2 0 -2 -1	Wave-numbers enclosed in brackets are estimated from the regularity of the system. In each case it has not been possible to measure the head
6163 5 57 8 6116 2 6110 3	8	16220 16235 16846 16361	B ₂ B ₁ A ₂ A ₁	61	75	-2 0 0 2	for some reason which is cited. Measured intervals (δn) , A_1-A_2 , B_1-B_2 , vary be-
57 ^{25 · 4} 21 · 5 56 ^{85 · 3} 56 ^{80 · 9}	2	17461 17478 17584 17598	B ₂ B ₁ A ₂ A ₁	60	75	1 0 0 1	tween 11 and 15; mean = 13. Mean measured separation A_1 - B_1 = A_3 - B_2 = 124.
55 ⁵⁰ ·0 45·9 55 ¹¹ ·9 55 ⁰⁷ ·5	8	18018 18026 18188 18152	132 131 142 141	61	76	1 1 2 3	
58 <mark>58 0</mark> 58 <mark>49 6</mark> 58 <mark>17 8</mark>	3	18676 18688 18601 18814	B ₂ B ₁ A ₂ A ₁	59	75	-1 -2 0 0	
5042 4 5089 1 5007 4	8	19826 19880 19951 19965	B ₂ B ₁ A ₂ A ₁	61	77	0 0 1 2	

Table I.—The Less Refrangible System (a)—continued.

λ. Wave- length (I.Å.).	Inten- sity.	n. Wave- number in vacue.	Designa- tion.	m.	p.	Δ# OC.	Bemarks.
4885 ·3 4855 ·2	2	20464 [20477] 20691 [20604]	B ₂ B ₁ A ₂ A ₁	5 9	76	$\left \begin{array}{c} -8\\ \hline 0\\ -\end{array}\right\}$	Feeble and confused.
47 ⁴⁶ ·2 47 ⁴⁸ ·8 47 ¹⁷ ·9	7	21064 21077 21190 21202	B ₂ B ₁ A ₂ A ₁	60	77	0 0 2 1	
46 ^{14 · 9} 12 · 0 45 ^{88 · 3} 45 ^{88 · 4}	10	21668 21677 21789 21 8 02	B ₂ B ₁ A ₂ A ₁	61	78	-2 -1 0 0	
4361 ·7 4841 ·4 4839 ·0	9	[22907] 22920 28028 28041	B ₂ B ₁ A ₂ A ₁	60	78	5 2 2	Confused by structure line from B ₁ of same band.
42 ⁴⁸ ·9 46·4 42 ²⁷ ·1 42 ²⁴ ·7	5	23529 23543 23650 23664	B ₂ B ₁ A ₂ A ₁	61	79	4 5 1 2	
41 ⁴⁵ ·1 48·1 41 ²³ ·6	6	24118 24180 24244 24256	B ₂ B ₁ A ₂ A ₁	59	78	-1 -2 1 0	
10 ^{87 · 0} 35 · 1 10 ^{16 · 7} 10 ^{14 · 6}	8	24764 24776 24889 24902	B ₂ B ₁ A ₂ A ₁	60	79	1 0 2 2	
38 ⁴⁸ ·5 46·9	5	25977 25988 [26104] [26117]	$egin{array}{c} B_2 \ B_1 \ A_2 \ A_1 \end{array}$	59	79	-5 -7 - }	Masked by structure lines CN bands (λ 8888 group).
3677 ·3 36 ^{62 ·2} 36 ^{60 ·1}	7	[27178] 27186 27299 27314	B ₂ B ₁ A ₂ A ₁	58	79	-5 -8 -1	Confused by structure line from B ₁ of same band.
35 ²⁵ ·9 35 ²⁴ ·1 35 ¹¹ ·4 35 ₀₉ ·6	6	28854 28868 26471 28485	B ₂ B ₁ A ₂ A ₁	57	79	0 1 -7 -6	
88 <mark>87 ·6</mark> 86 ·1 88 <mark>74 ·2</mark> 88 72 · 7	5	29511 29524 29628 29641	B ₃ B ₁ A ₂ A ₁	56	79	1 1 -6 -6	

Tal	ole II.—I	he L	ess Ref	rangi	ble Syste	m (a)	. Wave	-num	bers of	Head	s A ₂ .
p	79		78	-	77		76		75		74
77 1											
61	23650	1861	21789	1988		1818	18138	1792	16846		
	1239		128 9		1289		1238		1238		
60	24889	1861	23028	1838	21190	1814	[19376]*	1792	17584	1769	15815
	1215		1216		1215		1215		1217		
59	[26104]+	1860	24244	1880	[22405]1	1814	20591	1790	18801		
	1195										
5 8	27299										
	1172										
67	28471										
	1157										
56	29628										
	* Ba	nd not	develor	ecl.							

+ Masked by CN bands (A 3883 group).

I Feeble, confused by structure lines of strong band from B. = [22907].

The wave-numbers in brackets are estimated values.

In the discussion of the distribution of the bands it will therefore be sufficient to consider one—say, A2—of the four heads of each band. Table II shows the wave-numbers of the heads A2 arranged in groups similar to those of the bands of cyanogen,* and of silicon nitride.† Thus, the heads A₂ may be represented by a Deslandres equation,

$$n = A + B(m + \mu)^2 + C(p + \pi)^2$$

in which A, B, and C are constants, m and p take successive integral values for consecutive values of n in vertical and horizontal directions respectively, while μ and π are fractional terms. B and C are respectively equal to half the common differences in the progressions formed by the tabulated intervals (or "first differences") in the vertical and horizontal directions.

Adopting as the means of the "second differences" the values 20.40 and 23.70 (which are partly derived from the measures of the more refrangible system, β_{1}^{*}) the equation becomes

$$n_{A_2} = 11.85 (p + 0.04)^2 - 10.20 (m + 0.18)^2 - 12203.$$

The same equation will include the other three heads if the constant A be altered in accordance with the constant intervals 13 and 124. For the complete representation of System a the constant A takes the values:-

$$\begin{bmatrix} B_2 & \dots & & & -12327 \\ B_1 & \dots & & & -12314 \end{bmatrix} \begin{bmatrix} 13 \\ A_2 & \dots & & & -12203 \\ A_1 & \dots & & & -12190 \end{bmatrix} \begin{bmatrix} 13 \\ \end{bmatrix} \begin{bmatrix} 124 \\ \end{bmatrix}$$

^{*} Fowler and Shaw, 'Roy. Soc. Proc.,' A, vol. 86, p. 125 (1912).

⁺ III, p. 191.

[‡] See p. 129.

The values of m and p for the observed bands are shown in both tables, and the differences (Δn) between observed and calculated wave-numbers are given in Table I.

The More Refrangible System (β) .

This system has a close resemblance to the silicon nitride spectrum, the bands in each case having single heads. Data relating to all the bands observed in the more refrangible region are included in Table III whether they belong directly to System β or not, while in Table IV the wavenumbers of the heads in System β are arranged in a manner similar to that already indicated for System a. The bands are more numerous than in the less refrangible system, and the determination of the constants of the Deslandres formula is therefore rendered more exact.

Table III.—The More Refrangible Bands.

	3.	ystem /	8	n.		λ.	
narks.	Remarks	Δ× O-C	p.	m.	Wave- number in racuo.	e-length sity.	Wave-length (I.A.).
		ļ			28596	8	8496 0
					28760	4	8476 ·0
		İ			28886	3	8460 9
					29040	6	8442 6
		!			29672	4	8869 -8
		į			29813	4	8858 -3
		i			30267	6	3303 0
					30882	8	8290 5
	İ	1	70	59	80700	5	8256 .4
	Į	!			30841	6	8241 5
•		-1	71	60	81158	5	8209 1
					31278	6	3196 ·2
		0	69	57	81425	8	3181 -3
	[1	72	61	31612	6	8162 .5
	$\boldsymbol{\beta}_{1}$			-	81756	5	8145 1
	' '	1	70	58	81897	9	8184 -2
		ī	78	62	32078	8	3117 0
		-2	71	59	82869	10	8088 -5
	β ₁ .	_			82566	6	8069 8
	· •	-1	72	- 60	82848	8	8043 4
		_		7.	32940	4	3085 0
	β_1 .	1			88058	8	8024 1
d.	Head not developed.		70	57	[88073]		
		-1	73	61	38829	9	2999 -5
		-ī	71	58	33567	8	2978 -8
	ĺ	î	74	62	88816	6	2956 3
		-ī	72	59	84065	8	2984 .7
	\$ ₁ .	-		50	34881	6	2912 0
4	1.4	1	78	60	34569	10	2891 -9
1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 -			1 "	0.7	84650	5	2885 2
		-1	71	57	84744	2	2877 -4
	β ₁ .		'-		34848	7	2868 8
		0	74	61	85073	9	2850 4
d.	Head not developed.		72	58	[35262]	1 _	2000 A

Table III—continued.

λ.		n.	System 8.					
Wave-length	Inten	Wave-			1	Remarks.		
Wave-length (I.A.).	sity.	number			Δn	and the same of th		
(2.22).		in vacuo.	m.	p.	O-C.			
2826 ·8	8	85366				$\boldsymbol{\beta}_1$.		
2809 .7	8	35581	62	75	-1	· •		
2798 .7	8	35784	59	78	-2			
2767 · 7	6	36120	1	}) ;	β_{l} .		
ש: 2753	9	86811	60	74	0			
2747 .7	2	86388						
2748 5	6	36489	57	72	-1	4		
2726 9	6	36661	0.		١,	β_1 .		
2718 6	8	36841	61 58	75 73	$-\frac{1}{2}$			
2703 ·3 2686 ·9	6	36981 37207	93	13		β_1 .		
2675 ·2	9	37369	62	76	-3	P1.		
2672 -8	2	87408	\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	,,,				
2664 0	7	87527	59	74	-2			
2635 .7	2	37930		,	-	$\boldsymbol{\beta}_1$.		
2625 .4	8	88078	59	75	0			
2620 .3	3	88152	57	78	-7			
259 0 ·2	7	88507	1		1	β_1 .		
2587 '9	8	88630	61	76	0			
2581 ·6	8	88724	58	74	-2			
2558 .8	7	89070	-			$\boldsymbol{\beta}_1$.		
2551 2	10	89186	62	77	0			
2544 ·1	10	39295	57	75	0			
2542 4	6 6	39321		1		۵		
2518 ·4 2507 ·5	8	39775 89869	60	76	1	β_1 .		
2505 .3	6	39904	57	74	2			
2498 .7	4	40089	0.	' -				
2488 -1	4	41079		1				
		[40447]	61	77		Possibly present, but masked by N band (λ 2479, 3rd positive group).		
		40492	57	75		band (λ 2479, 8rd positive group).		
2486 9	10	41028	62	78	-1			
2433 ·2	8,	41086	59	76	0			
2427 -9	8	41175						
		[41669]	57	75		Masked by next strong band (λ2898 .8)		
2898 ·3	10	41684	60	77	2	Many has do superposed		
2864 -2	9	42085	{ 58 61	76 78	28	Two heads superposed.		
2881 ·1	8	42885	62	79	8,1			
2880 2	7	42902	59	77	2			
2299 9	8	48467	57	76	7			
2297 ·0	ŏ	48522	60	78	2			
		[44100]	58	77		Masked by next strong band (\$2264.6)		
2264 6	10	44144	61	79	1	,		
2268 · 2	. 6	44171			1	$oldsymbol{eta_2}$.		
2234 5	6	44789	59	78	2			
2282 4	2	44781			1	$oldsymbol{eta_{2}}_{\bullet}$		
2202 9	9	45881	60	79	0 .			
2199 6	4	45444		70		<i>β</i> ₂ .		
9176 ·3	8	45986	84	72	. 2	D		
2172 7	1 5	46011 46590	59	79	0	<i>B</i> ₂ .		
2145 8 2140 8	2	46697	103	10	"			
- ANDO G	**	40001	1	1	1			

Table IV.—The More Refrangible System (β) .

42865 1367 1267 1267 1267 1267 1268 1267 1267 1268 1267 1267 1268 1267 1268 1267 1268 1267 1268 1267 1268 1267 1268 1267 1268 1267 1268 1267 1268 127 1268 127 1268 127 1268 127 1268 127 1268 127 1268 127 1268 127 1268 127 1268 127 1268 127 1268 127 1268 127 1268 127 128 128 128 128 128 128 128 128 128 128 128 128 128 128 128 128 <th>•</th> <th></th> <th>78</th> <th></th> <th>11</th> <th></th> <th>26</th> <th></th> <th>75</th> <th></th> <th>74</th> <th></th> <th>73</th> <th>7.3</th> <th>17</th> <th></th> <th>7.0</th> <th>69</th>	•		78		11		26		75		74		73	7.3	17		7.0	69
1261 1262 1256 1256 1256 1256 1256 1256 1256 1256 1256 1256 1256 1717 31612 1236 1717 31612 3264 1236 1717 31612 3264 1236 1717 31612 3264 1236 1717 31612 3264 1236 1717 31612 3264 1236 1717 3264 1717 3264 1717 3264 1717 3264 1717 3264 1717 3264 1717 3264 1717 3264 1717 3264 1717 3264 1717 3264 1717 3264 1717 3264 1717 3264 1717 3264 1717 3264 1717 3264 1717 3264 1717 3264 3264 3264 3264 3264 3264 3264 3264 3264 3264 3264 3264 3264 3264 3264 3264 3264 3264 3264	1 1862 410	410	8	1837		1817	37369	1788	35581	1765	33816	1743 3	2073					
1237 1239 1239 1237 1238 1237 1238 1240 1236 1238 1239 1238	1269 12	=	29		1261		1262		1260		1257		1256					
1237 1239 1237 1238 1240 1236 1236 1236 1236 1236 1236 1236 1237 1217 1216 1217 1217 1217 1216 1217 1217 1216 1217 1217 1217 1216 1217 1217 1217 1217 1217 1217 1217 1217 1217 1217 1217 1217 1217 1217 1217 1217 1217 1217 1217 1197 <th< td=""><th>1859 42</th><td>3</td><td>1285</td><td></td><td>[40447]*</td><td>1817</td><td>38630</td><td>1789</td><td>36841</td><td>1768</td><td>35073</td><td>1744 3</td><td>3329 1717</td><td></td><td></td><td></td><td></td><td></td></th<>	1859 42	3	1285		[40447]*	1817	38630	1789	36841	1768	35073	1744 3	3329 1717					
41084 1815 39869 1791 38078 1767 36311 1742 34569 1721 32848 42902 1816 41086 1791 39295 1768 37527 1743 35784 1719 1217 1198 1199 1197 1197 1197 1197 1197 1197 1182 1177 1180 1177 1180 1177 1187 1177 43467 1798 14169] 1765 39904 1752 38158 1713 36439	1237	-	237		1237		1239		1287		1238		1240	1236				
42902 1816 1217 1216 1216 1215 1217 42902 1816 1791 39295 1768 37527 1743 35784 1719 34065 1198 1199 1197 1197 1197 1197 1197 1 44100]† 1815 42285 1793 1794 1794 1797 1197 1 182 1777 1180 1771 1177 1177 1177 1177 43467 1796 [41669]§ 1765 39904 1752 38152 1713 36439	1859 4	4	3522	1838		1815	39869	1921	38078	1767	36311	1742 3	4569 1721		1695 31153			
42902 1816 41086 1791 39295 1768 37527 1743 35784 1719 34065 1198 1199 1197 1197 1197 1197 1197 1197 1 [44100] 1815 1793 [40492] 1768 38724 1743 36981 1779 [35262] 1 1182 1177 1180 1177 1187 1177 1177 43467 1798 [41669] 1765 39904 1752 38152 1713 36439	1218		1217		1218		1217		1217		1216		1215	1217	1216			
1198 1197 1197 1197 1197 1197 1197 1197	18604	-	4739	1837		1816	41086	1791		1768	37527	1743 3	5784 1719	34065	1696 32369	6991	30700	
45936 1836 [44100]† 1815 42285 1793 [40492]* 1768 38724 1743 36981 1719 [35262]‡ 1695 33567 1670 31897 1182 1177 1180 1171 1177 1176 43467 1798 [41689]§ 1765 39904 1752 38152 1713 36439 1695 34744 1671 [33073]‡ 1649 31424			1197		1198		1199		1197		1197		1197	1197	1198		1197	
36439			45936		[44100]+	1815	42285	1793	[40492]*	1768	38724	1743	16981 1719	[35262]‡	1695 33567	1670	31897	
36439							1182		1177		1180		1711	1177	7711		1176	
							43467	1798	[41669]§	1765	39904	1752	8152 1713		1695 34744	1671	[33073]‡	1649 31424

* Probably present (A 2472, 2469) but masked by N band (A2479, 3rd positive group).

† Masked by strong band (44144).

‡ Head not developed.

§ Masked by strong band (41684).

It is at once evident that the intervals 1237... and 1861... of Table II occur also in Table IV, and that the common differences in the progressions have the same two values in both systems of bands. The constants of the formulæ have, therefore, been evaluated from observations of the two systems jointly, and the same values adopted for both. The mean "second differences" in the rows and columns of Tables II and IV are 23.70 and 20.40, and the equation representing System β is

$$n_B = 11.85 (p + 0.04)^2 - 10.20 (m + 0.18)^2 + 8291,$$

in which m and p take the integral values indicated in Tables III and IV.

The ranges of m and p are very nearly the same in the two systems. Thus it results that the equations differ only in the values assigned to the constant A, *i.e.* four suitable shifts of System β (or a portion of it) bodily on a scale of wave-numbers will suffice to reproduce the quadruple head System α .

Subsidiary Systems.

In addition to the two chief systems of bands (a and β) already considered, there is evidence of other systems which are only comparatively feebly developed. These, however, are not entirely independent of the main System β , since the heads are single, and the intervals and second differences are of the same orders of magnitude. Two such subsidiary systems have been recognised, and may conveniently be designated β_1 and β_2 . The positions of these bands are included in Table III, and their inter-relations are indicated in Table V.

Table V.

System	B_1
A THE PARTY OF THE	~ 1

39070	1863	37207 1300	1841	35366 1295	1816	[33550]* 1298	1794	31756 1802		
		38507 1268	1846	36661 1269	1813	34848 1272	1790	33058 1273		
		39775	1845	37930	1810	36120	1789	34331	1765	32566
			* h	facked by	band 8	RKR7 of Strate	m A			

System \$2.

44171 1273 45444 1258 48607 1916 44781 1230 46011

Origin of the New Bands.

In the course of the experiments on boron trichloride in active nitrogen, a white solid substance was deposited on the inside of the afterglow tube. With a view to gaining some evidence as to the origin of the new bands this substance was removed and submitted to a Nessler test, which amply proved the presence of nitrogen in the deposit.

In order to investigate the possibility of chlorine being necessary for the development of the bands, the vapour of another boron compound not containing chlorine was substituted for the trichloride. The compound selected was methyl borate (CH₃)₂BO₃, a colourless liquid, not so volatile as the trichloride—boiling point 72° C. It was prepared by passing the vapour of the trichloride into pure methyl alcohol cooled in a freezing mixture. Excess of HCl, one product of the reaction, was removed by bubbling dry air through the resulting liquid for some time, and the product was further purified by fractional distillation. The glow produced by the introduction of this substance had not the pale blue-green colour of the former glow, but was obviously contaminated by the purple cyanogen glow. The spectrum consisted of the boron lines, the cyanogen and nitrogen bands, and the new bands under consideration. It therefore results that chlorine does not enter into the question.

The latter conclusion was confirmed by an observation of the spectrum of boron trichloride in a vacuum tube provided with a quartz window. The vapour was obtained in such a state of purity that no nitrogen bands were present. The new bands were entirely absent.

It is evident, therefore, that while boron and nitrogen are concerned in the development of the bands, no other element appears to be necessary for their production. They have therefore been attributed to boron nitride.

A search for the nitride bands in the green flame produced by methyl borate in the bunsen flame proved to be unfruitful. This spectrum contains only the oxide bands as observed by Weith,* and later by Eder and Valenta.†

The non-disruptive spark spectrum of boron was also investigated with a view to determining whether the nitride bands were produced. This experiment was rendered possible by the kindness of Sir William Crookes, who supplied a sample of the melted boron (prepared by Dr. Weintraub[‡]) used by him in 1911 in his work on the boron line spectrum. Photographs of the spectrum of the spark in an atmosphere of nitrogen showed no trace of the nitride bands, even when sufficient self-induction was included in the circuit

^{* &#}x27;Chem. Centralbl.,' vol. 7, p. 164 (1876).

^{† &#}x27;Denkschr. Wien. Akad.,' vol. 60, p. 467 (1893).

^{† &#}x27;Trans. Amer. Electrochem. Soc.,' vol. 16, p. 165 (1909).

to develop strongly the band spectrum of nitrogen. In an atmosphere of oxygen the oxide bands were similarly absent, even with the self-induction in the circuit. Lecoq de Boisbaudran,* however, observed these bands in the spark, using a hydrochloric acid solution of boric acid. Eder and Valenta, and Hagenbach and Konen, have also observed the oxide bands in the uncondensed spark spectrum of boric acid.

Occurrence in the Arc.

If boron nitride is the true origin of the new spectrum, then since this compound is formed when nitrogen is passed over heated boron, the bands would be expected to occur in the boron arc in air or nitrogen, just as the cyanogen bands are developed in the carbon arc. Although much work has been done on the arc spectrum of boron compounds (chiefly boric acid and anhydride), the only bands which have been recorded in addition to the oxide bands already referred to above are some observed by G. Kühne.† Kühne photographed the flame and arc spectra of boric acid by means of the 21-ft. concave grating at Bonn, and measured structure lines emanating from four single heads, which are stated to be at λλ 5022·19, 5046·79, 5515·02, 5552·98. These degrade to the red, and are designated by Kühne A, B, C, D, respectively. The series from A and C were found to consist of single lines and those from B and D of doublets. The figures in the boron nitride spectrum (Table I) nearest to those quoted above are respectively

$$50_{07\cdot5}^{10\cdot9}$$
, $50_{39\cdot1}^{42\cdot4}$; $55_{07\cdot5}^{11\cdot9}$, $55_{45\cdot9}^{50\cdot0}$.

belonging to two of the strong bands of System α . The agreement, however, is not near enough to do more than barely suggest identity. Moreover, while the nitride heads are double, Kühne's are described as single, and no mention is made of other heads having wave-lengths correspondingly near other strong bands of the nitride system.

The arc spectrum of boric oxide was photographed with the same two spectrographs as were used in the afterglow experiments. The headless oxide bands are the most prominent feature of the spectrum (Plate 2, strip 1). Cyanogen bands and lines due to impurities are also present, and superposition of afterglow photographs led to the detection of the strongest of the nitride heads of System α in the arc spectrum.

The intervening fainter heads of System a have not been detected in the arc owing partly to the confusion caused by the presence of the oxide

^{* &#}x27;Spectres Lumineux,' p. 193, Paris, 1874.

^{† &#}x27;Zeitsch. f. Wiss. Photog.,' vol. 4, p. 173 (1906).

spectrum, and also, perhaps, to certain modifications of intensity presently to be described in connection with the more refrangible bands.

On none of the arc photographs was it possible to detect any heads near the four positions given by Kühne other than those already mentioned. In each case the present measurements result in smaller wave-lengths than Kühne's corresponding value. A possible explanation of the discrepancy, assuming the identity of the bands, would be that, on account of the high dispersion employed and the ill-defined nature of the heads in the arc, Kühne misjudged the positions of the heads A_2 and B_2 , and entirely missed the second heads, A_1 and B_1 , of the doublets.

Similar results were obtained in the case of elemental boron in the are in air, and in nitrogen; in the latter case the oxide bands occurred with relatively diminished intensity but were never entirely absent, as would be expected if oxygen could be totally excluded. Photographs of the elemental boron arc in an atmosphere of oxygen were consistent with the nitride origin of the new spectrum; for, although the less refrangible system was feebly present, the more refrangible bands were generally absent. The experiment, however, was not regarded as very important, as with the arrangement employed it was uncertain whether all the air was displaced by oxygen.

In the far ultra-violet region, not confused by the superposition of other bands, the difference between the nitride bands (System β) in the arc and the afterglow is mainly one of intensity. As in the visible region, the strong heads are well defined in the arc, but in addition to these the intervening feebler heads are sometimes discernible. In the afterglow the heads are much better defined, and the structure lines fall off in intensity much more rapidly as their distance from the head increases than is the case in the arc. Thus the feebler heads stand out distinctly above the structure lines from the preceding strong head in the afterglow; while in the arc they are almost entirely masked by the intense structure lines.

This contraction of the bands in the afterglow relatively to the arc may be a direct result of the diminished pressure. A similar contraction is observed in the cyanogen bands as produced in the electric discharge through a cyanogen tube, compared with the same bands developed in the carbon arc at atmospheric pressure.* Cases are known, also, in which bands are shorter in the afterglow than the same bands in the electric discharge, e.g. the nitrogen bands of group γ .+

^{*} Fowler and Shaw, loc. cit., Plate 7.

[†] I, Plate 10, fig. 3b.

Comparison with Carbon and Silicon.

Boron, the only non-metallic element in its group (III) in the Periodic Classification, is well known not only to have similar general chemical properties to the other elements (aluminium, gallium, etc.) of the same trivalent group, but also to bear some striking analogies to the tetravalent non-metals, carbon and silicon, of the next group (IV).

The behaviour of the vapours of its compounds in the afterglow is now shown to be a new instance of this resemblance. Compounds of all three elements develop the spectra of the products of their reactions with the active nitrogen, and not merely the spectrum of the substance introduced, or the line spectrum of the element itself, as in the case with the tetrachloride of titanium,* a metal of the earbon group. Moreover, in each of the three cases under consideration the product is the nitride of the element. Although the spectra of the three nitrides may each be analysed into groups and represented by equations, of the general type given by Deslandres, yet marked differences in the constitution of the bands themselves occur in the three spectra. Silicon nitride has the simplest spectrum, consisting of one system of bands with single heads degraded towards the red. Thus it resembles the more refrangible system (β) of boron nitride. The quadruple head system (α) of boron nitride has no real counterpart in the nitrides of the other elements. Of the two cyanogen systems, the less refrangible has triple heads degraded towards the red, and the more refrangible (comprising the well-known groups at λ 4216, 3883, and 3590) has single heads degraded in the opposite direction. Both these systems are well developed in the afterglow together with the associated "tails."+

Summary.

- 1. The interaction of active nitrogen and boron trichloride, or methyl borate, develops a band spectrum extending from λ 6371 to at least λ 2140, with well defined heads degraded throughout towards the red.
- 2. The new spectrum consists mainly of two distinct systems, in the less refrangible of which each band consists of four heads, forming two close doublets. The more refrangible system has single heads, and thus resembles the silicon nitride spectrum described in a previous paper.
- 3. The wave-lengths of the heads have been measured, and the wave-numbers in each system have been classified and represented by formulæ in the usual manner.
 - 4. Chemical and spectroscopic evidence has established that the origin of

^{*} III, p. 192.

[†] II, p. 115.

the spectrum is boron nitride. Boron, carbon, and silicon compounds are thus alike in developing nitride spectra in the nitrogen afterglow.

5. The boron nitride bands, like those of cyanogen, are produced in the electric arc spectrum, where they occur together with bands of the oxide.

I wish to express my obligations to Prof. Strutt for suggesting this work to me, and for again placing his large oil-pump at my disposal; and to Prof. Fowler for his valuable assistance in the course of the work. My best thanks are due also to Sir William Crookes for supplying me with the fused boron used in the spark experiments, and to Mr. H. V. A. Briscoe, B.Sc., of the Chemical Department of the Imperial College, for his assistance in the preparation of the boron trichloride and methyl borate.

DESCRIPTION OF PLATE.

Strip 1. Boron are, showing the wavy, headless exide bands and the strongest nitride heads (faintly).

Strips 2-6. Boron trichloride in active nitrogen, showing the nitride bands.

2, 3, and 4. Less refrangible system (a).

5 and 6. More refrangible system (β), and bands of subsidiary systems (β_1 and β_2). Impurities—Sn lines, Hg line (λ 2536), and CN bands.

Hermann's Phenomenon.

By George Stanley Walpole, D.Sc., F.I.C., Wellcome Physiological Research Laboratories, Herne Hill, London, S.E.

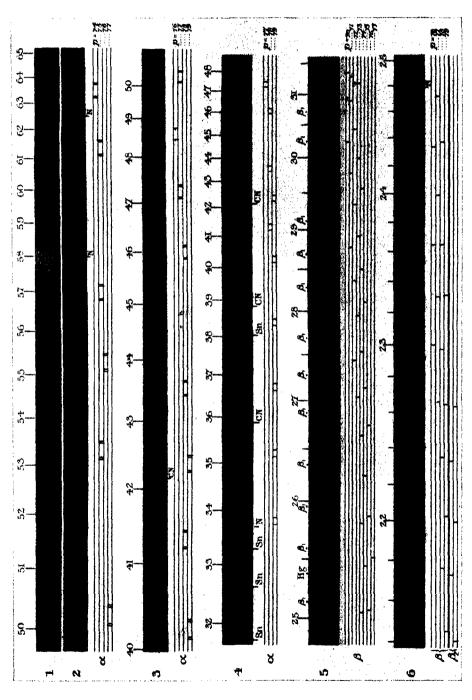
(Communicated by Prof. F. G. Donnan, F.R.S. Received November 17, 1914.)

In 1887, Hermann* published an account of some experiments from which he drew the conclusion that when an electric current passed from a dilute solution of a salt, such as sodium sulphate, to one more concentrated, a liberation of acid took place at the boundary layer between the two fluids; also, that when the current passed in the opposite direction alkali was liberated at the same place. His experimental difficulties were considerable, but the facts were firmly established, though it is only to be expected that their repetition and amplification to-day should suggest another interpretation to that put forward 27 years ago.

Strangely enough, although these phenomena were cited by early physio-

^{* &#}x27;Göttinger Nachrichten,' 1887.





logists as affording an explanation of the "electrical taste,"* they have quite escaped all the later text-books and articles on physico-chemical subjects. Rosenthal's experiments, which showed that the "electrical taste" was not to be attributed directly to electrolytic phenomena, may have led to a general but mistaken impression that Hermann's observations were faulty. In explaining the habits of certain free-swimming protozoa, however. Dale has attributed the directive stimuli to these boundary effects. The cogency of these speculations is in striking contrast to the earlier applications of Hermann's experiments to physiological problems. In a paper on the cataphoresis of ferments, too, V. Henri has alluded to the liberation of alkali and acid at the boundaries of the ferment solution and distilled water when an electric current is passed. This, as he remarks, cannot be avoided by the use of non-polarisable electrodes, but may be overcome by dialysing the enzyme solution until it has the same conductivity as the distilled water employed. It may be pointed out, in passing, that this undesirable restriction to the experimental conditions is not necessary; it is only essential that the specific conductivities of the two solutions should be the same. But, since the published work in which this precaution has not been taken would otherwise be not properly understood, it was decided to investigate the significance of these boundary complications in their relationship to transport experiments generally.

This enquiry, the results of which are discussed elsewhere, involved experiments made to confirm and amplify Hermann's original observations, and establish them as far as possible on a quantitative basis. A rational explanation of them in terms of the hypothesis of electrolytic dissociation resulted, and the matter of this curious phenomenon assumed a sufficient interest to suggest its separate publication.

Apparatus and Method of Experiment.

For all the experiments described in this communication a transport apparatus made entirely of glass in one piece was used. The preliminary observations which led to its permanent adoption have not been described; where they were instructive they have been repeated under the better conditions afforded by this improved arrangement.

A rigid wooden stand screwed to the bench held the apparatus. The fitting was done carefully once and for all so that it could at any time be removed for filling, cleaning, etc., and replaced in exactly the same position.

The dimensions were chosen so that after the passage of the current reasonably large volumes of the fluid are available for examination. The

^{*} Biedermann, 'Electro-physiology,' vol. 2 (1908).

bore throughout was 10 mm., except at the taps, where it was 9 mm. Full-bore taps could not be obtained. The diagrams represent in elevation and in section the apparatus ready for an observation. It has been filled and the current is about to be turned on.

The filling of the apparatus takes only a few minutes; the problem is

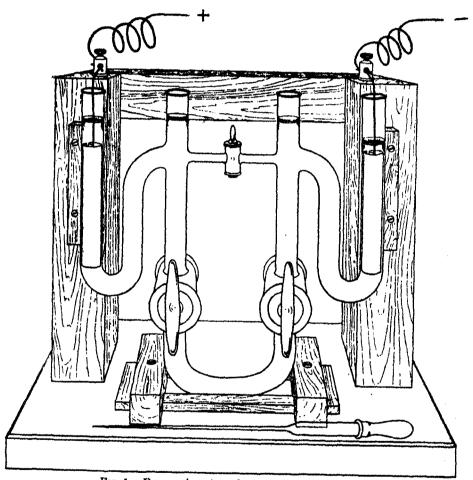


Fig. 1.—Perspective view of apparatus. (Half scale.)

simply to introduce four fluids, indicated in the sectional drawing, in such a manner that the boundary layers between them are sharply defined, and occupy certain positions which are exactly the same in consecutive experiments. After taking it in the hand with all three taps open, and rinsing it out with distilled water, the tube M and the lower parts of C and D (fig. 2), are rinsed, and then filled, with the "middle fluid." Any stray air bubbles

clinging to the glass are gently removed and the large taps shut. The fluid which is to occupy C and D is now used to rinse the excess of "middle fluid" out of the apparatus, which is then placed in position in the wooden stand.

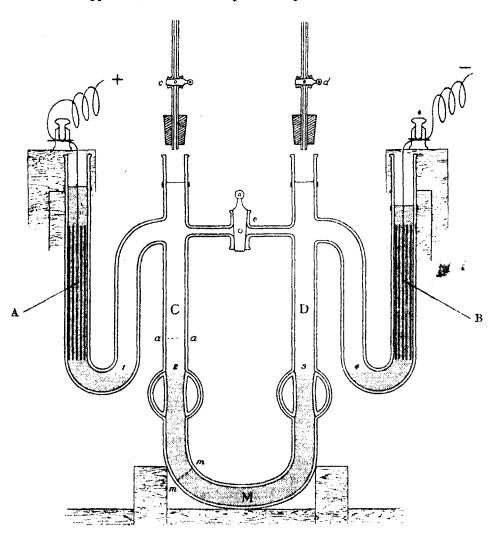


Fig. 2.—Section of apparatus. (Half scale.)

A. Silver anode in normal sodium chloride. B. Copper cathode in cupric chloride.

"Side tube fluid" is poured in until it reaches a mark 15 mm from the top of one of the four upright tubes. The small tap e is open, and by a little manipulation any air bubbles in this small transverse tube are removed. Into the tops of the tubes C and D rubber stoppers are introduced each carrying a

glass tube fitted with an open stopcock. These stopcocks are marked e and d. All three small taps c, d, and c, are now closed, and from the anode and cathode limbs as much fluid withdrawn by means of a suitable pipetting arrangement as is possible without allowing air to run back into C or D. When this is done, a spiral silver sheet anode connected by a silver wire to the positive binding screw is introduced into the anode limb, and normal sodium chloride run in slowly until its meniscus reaches a certain mark. This mark is so arranged that when air is let in through c the column in C does not move, for it balances that in the anode limb exactly. In a similar fashion the cathode limb is filled with 5-per-cent, copper chloride solution round a copper electrode. The stopcocks c, d, and c, are now opened and the rubber stoppers carefully removed. The large taps are opened with a slow even motion and e is shut. The result is that the four fluids are arranged as it was desired with four sharp boundaries in the positions indicated in the sectional drawing. The position of the "middle tube fluid" and the "electrode fluid" are shown by stippling. The "side tube" space is left clear. It should be noticed that the position of the apparatus in its wooden frame has been carefully adjusted so that the tops of the plugs of the large taps are in the same horizontal plane. The adjustment is checked by filling M and the bores of both taps with a coloured fluid and noting the position of the two meniscuses relative to the plugs of the taps. The two binding screws are now put in connection with a direct lighting main, say, at 115 volts. It is, of course, one essential condition of these experiments that the actual current passed be so small that even at this voltage the rise of temperature due to the heat generated in the apparatus is insufficient to cause any appreciable convection currents.

After disconnecting again from the main the large taps are turned off very slowly to prevent mixing of the solutions by eddy currents, and the distribution of acid and alkali at the boundaries is investigated by one or other of the various simple devices which suggest themselves at once. A "medicine dropper" made of hard glass and drawn out to a long fine capillary is convenient for introducing strong indicator solution at the desired point, for removing liquid from a given region, or for mixing small quantities of fluid by drawing them up successively and delivering them into a common vessel after the manner of the bacteriologist.

If, for example, in an experiment where the "middle fluid" is 5-per-cent. sodium chloride and the "side tube fluid" 0.05-per-cent. sodium chloride, azolitmin dissolved in 0.05-per-cent. sodium chloride be floated upon the meniscus of A and B, it will in a few minutes diffuse and fall down to the four boundaries and demonstrate that, though the liquid in between has

stayed neutral, acid has been liberated at the boundaries 2 and 4, counting from left to right, where the current has passed from a dilute to a concentrated solution; and alkali has been liberated at boundaries 1 and 3, where the current has passed from a solution more concentrated to one Moreover, the coloured fluid will come to rest and spread more dilute. out at a certain depth where it reaches a layer of fluid, of a density greater The actual position of the clean-cut lower horizontal boundary of the now coloured fluid in C and D is the limit of the upward diffusion of the more concentrated salt solution, and will depend only upon the duration of the experiment. The position of this upper limit is the same whether the current is turned on or not. The effect of the current is seen in that the lowest fraction of a millimetre of the azolitmin-tinted "side tube fluid" is red in one case and blue in the other, instead of being uniformly neutral in colour. The appearance can only be taken as signifying that the uppermost limits of the region of acid and alkali liberation are horizontal and sharply defined; they coincide with the limit of salt diffusion upward, and are to be found even several hours after the opening of the large taps, only a millimetre or two above the original position of the boundary.

In all the experiments described later, alkali and acid liberations at boundaries 1 and 4 respectively were observed, but as their discussion, except so far as the considerations referring to boundaries 2 and 3 apply, is irrelevant to this investigation they will not be referred to again.

As the result of considerable experience, it may be stated of experiments in which the connection to the 115 volt main lasts for four hours only, that a first measurement of the amounts of acid and alkali liberated may be made in the following manner. The large taps are closed very carefully, both electrode fluids are sucked out with a pipette, so that the column of liquid vertically above each tap is isolated, azolitmin solution is introduced into C and D, and the liquid stirred. The amount of azolitinin solution used is the same for each experiment, and the colours assumed after stirring indicate the quantities of acid and alkali developed. Subsequently, search for acid and alkali in the bores of the taps may be made, but under these conditions little will be found. The explanation is simple when it is recognised that the sites of development of acid and alkali are the boundaries of the concentrated and the dilute solution, and that these move upwards about 4 mm. in four hours by the ordinary process of diffusion. To detect the extremely minute traces of acid and alkali formed when the experiment has only run a few minutes, it is advisable to remove all the neutral supernatant fluid from the side tubes, except the lowest 10 mm., before adding indicator and stirring. A more complete description of the shape and position of the region in which a change of reaction is observed, and the actual titration of the amounts of acid and alkali developed, will be given later.

1st Series of Experiments. The amounts of acid and alkali liberated bear no relation to the amount of current passed.—Using as "middle fluid" any sodium chloride solution from 0.01 per cent. to 5 per cent., the amounts of acid and alkali obtained at the boundaries were the same, as nearly as could be judged, as long as the "side tube fluids" were distilled water. Also, using 5-percent. sodium chloride as "middle fluid" and as "side tube fluid" a 0.05-percent. solution of the same salt the result was still the same, though of course the current passed was many hundred times greater in this case. In fact, the amounts of acid and alkali liberated at 100 volts in four hours were independent of the concentrations of the "middle fluid" and "side tube fluid" as long as the former conducted electricity at least 100 times as well as the latter. To avoid heat liberation and subsequent convection currents the "side tube fluid" was never more concentrated than 0.05 per cent.

2nd Series. The acid, no matter what neutral salt be used, is always liberated where the current passes from the more dilute to the more concentrated solution; the alkali is always liberated where the current passes from the concentrated solution to that more dilute.—In this series of experiments a number of neutral salts were examined. Five-per-cent. solutions were used as "middle fluid"; the same solutions 100 times diluted were taken to fill the "side tubes." In all cases acid was found at the left and alkali at the right boundary.

The neutral salts chosen were examples cited of the following groups:—

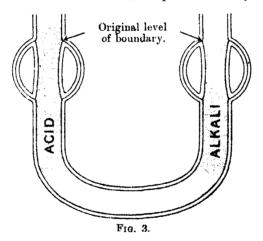
- (a) Those whose anion and cation have approximately equal migration velocities, e.g., KCl, KI.
- (b) Those whose anion is the faster ion, c.g., MgSO₄, K₂SO₄, NaCl, AgNO₃.
- (c) Those whose cation is the faster ion, e.g., KClO₃.
- (d) Those whose anion migration ratio increases with dilution, e.g., MgSO₄, NaCl, KCl, KI.
- (e) Those whose anion inigration ratio decreases with dilution, e.g., AgNO₃.

3rd Series. Other conditions being the same, a constant amount of acid and alkali is liberated, no matter what neutral salt be used.—The individual experiments of the second series above were done in pairs. Two neutral salts were taken, and the 5-per-cent. and 0.05-per-cent. solutions of each prepared from the same sample of distilled water. They were filled into two similar transport apparatus, and connected to the same 115 D.C. main in parallel for the

same time, and then examined in the same manner. The salts were chosen from groups a, b, c, d, e above, in various combinations, but there was no indication that the effect was greater in one case than in another.

4th Series. Experiments to determine the configuration and position of the zones of acid and alkali liberation.—The upper limits of the two zones in which a change of reaction has occurred have been discovered (p. 139, paragraph 1); they coincide with the upper limits of the diffusion of the salt solution. The lower limits are found by removing fluids at different levels and testing. The taps are of assistance in doing this. The operations are tedious, but with a hard glass medicine dropper drawn out to a long fine point trustworthy information can be obtained. It is found that the acid and alkali spread down more and more, as the duration of the experiment is increased, presenting an irregular diffusion front.

The state of affairs after eight hours at 220 volts, when the two fluids are water and 5-per-cent. sodium chloride, is represented in fig. 3.



5th Series. The quantities of acid and alkali developed increase with time and then become constant.—From what has been said in the last paragraph it will be anticipated that, as the rate of acid and alkali production is very small, there will soon come a time when they diffuse downwards away from their source as rapidly as they are liberated, and that their diffusion fronts will meet. Neutralisation and consequent disappearance of the acid and alkali will occur somewhere near the middle of M as rapidly as they originate near the bottom of the side tubes.

There is every indication that this is what takes place. At 220 volts, with the apparatus of the dimensions given, this maximum is reached in about 36 hours. The quantities of acid and alkali found in the two regions increase

steadily up to this time. The time taken to reach this maximum would naturally be longer, and the maximum quantities of acid and alkali obtainable would be greater, in an apparatus made with a longer middle tube.

6th Series. Measurement by titration of the quantities of acid and alkali liberated.—The quantities are extremely small—so much so that without preliminary experience their measurement could not be undertaken. In the particular experiment chosen as affording the greatest opportunity of exact quantitative investigation, 0.25-per-cent, sodium chloride solution was surmounted by "conductivity" water. This small concentration of salt was used in the middle fluid in order to minimise the effect of the neutral salt on the indicator in the subsequent titration.

Using 115 volts, the duration of the experiment was limited to five hours, as it was known that in this time the lower limits of the acid and alkaline zones would not extend down far enough to escape their subsequent removal intact. At the end of the experiment, to avoid undue dilution of the acid and alkali, the taps were closed and the "side tube fluid" was removed except that occupying the lowest 20 mm, above the taps on either side. This was done by removing first the electrode fluids, so that the columns of liquid vertically above the taps were isolated, and then by the judicious use of a long, fine-pointed pipette. Then, opening the taps one at a time and closing either before opening the other, 4 c.c. of fluid were removed by pipette from each side of the apparatus. The experiment was performed in duplicate with two complete sets of apparatus, so that 8 c.c. of alkaline fluid and 8 c.c. of acid fluid were obtained. These two portions of 8 c.c. could, as a result of the preliminary experiments detailed, be relied upon to contain respectively the whole of the acid and alkali liberated as a result of the passage of the current. As they contained only 0:13 per cent. (circ.) of sodium chloride, the effect of neutral salt on the indicator could be neglected. Four beakers were taken :--

- (a) 8 c.c. fluid from left-hand limb.
- (b) 8 c.c. fluid from right-hand limb.
- (c) 8 c.c. fluid Sörensen N/15 phosphate mixture (6.5 c.c. Na₂HPO₄+ 3.5 c.c. KH₂PO₄).
- $\binom{(d)}{(e)}$ 8 c.c. of same water as used to fill the apparatus.

To each was added just enough neutral red to colour the fluid a practicable amount. This indicator was chosen because the P_{π}^+ range over which it shows colour change is small and extends on both sides of absolute neutrality. The tubes (e), (d), and (e) matched exactly. The addition of one drop of 0.001 N

caustic soda to (d) or 0.001 N hydrochloric acid to (e) caused them to turn permanently yellow and red respectively. The contents of beaker (a) was redder than that of (c). After the addition of 0.20 c.c. of 0.001 N caustic soda to (a), they matched in colour; but (a) slowly developed a pink tinge again. By adding a further 0.10 c.c., (a) remained yellower than (c) for some minutes. The titration of the acid liberated in each apparatus was, therefore, about 0.10 c.c., and certainly less than 0.15 c.c. of 0.001 N solution. Many experiments were made to account for this small, but in proportion to the titration volumes very large, time change. It was not understood. The control experiments described above are evidence that it is due neither to atmospheric carbon dioxide nor the reaction inertia of the indicator. A special experiment was made, leaving the fluids in the apparatus for 24 hours without turning on the current. It showed that it could not be attributed to alkali from the glass.

The titration of (b) to the same tint as (c) was certainly more sharp. It required about 0.10 c.c. of 0.001 N hydrochloric acid. The alkali liberation in each apparatus was therefore about 0.05, and certainly less than 0.08 c.c. of 0.001 N solution.

Theoretical Interpretation of the Results Observed.

From the evidence available at this stage it is legitimate to draw the conclusion that these boundary phenomena cannot be attributed to any property of neutral salt solutions not common to them all. Since the most obvious electrochemical property common to all neutral salts in solution is that of enhancing enormously the specific conductivity of pure water when dissolved therein, it is not surprising that this, and the hypothesis of the dissociation of water into H' and OH' ions, should supply the greater part of the explanation sought. It may be noticed at once, therefore, that in either limb of the apparatus as filled for any one of these experiments there is a column of highly conducting solution (e.g. 5-per-cent. sodium chloride solution) with a column of very feebly conducting solution (e.g. 0.05-per-cent. sodium chloride solution or, even better, pure water) above it. The columns of liquid are placed in series and in electrical connection with two points at a different electrical potential. It follows, therefore, that the strength of the electrostatic field, which is expressed as a change of potential per unit length, is great above the boundary and small below it. The field is downward on the left-hand side of the apparatus and upward on the right.

Since the contents of the U-tube are at the commencement neutral throughout, the hydrogen and hydroxyl ions per cubic centimetre are equal in number and evenly distributed both in the dilute and in the concentrated

solution.* When the current is turned on the migration of the hydrogen ions commences in the direction of the field, while the hydroxyl ions move in the opposite direction. Migration is rapid in the dilute and slow in the strong salt solution. Hence at the left-hand boundary the number of hydrogen ions arriving in unit time from above is many times greater than the number leaving in the same time in a downward direction; the number of hydroxyl ions leaving in an upward direction is, in similar fashion, greater than the number arriving from below. The resulting excess of hydrogen ions over hydroxyl ions accounts for the observed "acid" at this place. The development of alkali at the right-hand boundary is attributed to the accumulation of hydroxyl ions in excess of the hydrogen ions at this place by the converse process. There is one point which cannot be overlooked. The product of the H' and OH' concentrations at any point in the solutions at any time must be k_w . If the concentrations of H' and OH' resulting from the original concentrations plus ionic migration do not satisfy this relationship, then it can be assumed that a dissociation of water takes place till the relationship is again established. The dissociation may be positive or negative, but, since H' or OH' ions are liberated or disappear in equal amounts by this means, it cannot abolish the excess or deficiency of H' or OH' ions per cubic centimetre set up as a result of ionic migration in the manner suggested,

As pointed out by Dr. C. J. Martin while discussing this explanation, an accumulation of H or OH ions in any region, though a convenient expression, cannot be regarded as the whole of the phenomenon. Ions such as Cl or Namust be attracted electrostatically from other regions to balance them. With this addition the picture of the condition of affairs is complete, and the development of "hydrochloric acid" and "caustic soda," both, of course, highly ionised, is accounted for.

On the same lines may be explained why the upper layer of the region of changed reaction is sharply defined while the lower layer is not. Imagine at the left-hand boundary, where the diffusion front of the strong salt solution is a well marked horizontal layer, a hydrogen ion diffusing upwards ahead of its companion Na', Cl', and OH' ions. It passes into a field of high intensity and is immediately forced down again. No such hindrance is met in its natural diffusion downwards; it has, in fact, a small force helping it. This, coupled with its high natural velocity of diffusion, accounts for the discovery of acid, even after a few hours, a considerable distance below the original position of the boundary.

If these explanations of the phenomena observed are accepted, further

^{*} The effect of the neutral salt on the dissociation constant of water need not here becomidered.

problems immediately present themselves as to the finer mechanism of these changes of reaction and the energy changes at the boundaries. Their complete solution demands mathematical treatment of an advanced order.

An attempt at calculating the gross amounts of acid and alkali developed, however, say in the experiment described under the heading 6th Series, may be made at once—assuming that the explanation of the phenomena observed is correct and complete. The region of acid development, which it will be convenient to consider first, is totally included between the sections aa and mm of the apparatus. At both of these sections the fluid is neutral, even at the end of the experiment. The volume included is 4 c.c. The total gramme equivalents of ionised hydrogen which pass in across aa during the whole time of the experiment may be written at once

$$10^{-3} \times 10^{-P_{\mathrm{H}}^{+}} \times tvae,\tag{1}$$

where t is the time for which the experiment has run in seconds; v, the velocity of the hydrogen ion under unit potential gradient; a, the area of the cross-section; and c, the fall of potential per unit length across that section. Similarly since the migration velocity of the OH' ion is 18/33 that of the H' ion, the total gramme equivalents of OH leaving the region by passing upwards across aa, is

$$10^{-3} \times 10^{-14\cdot 14 + P_H^+} \times t \times \frac{18}{33} vae.$$
 (2)

The migrations of H' and OH' ions past the section mm are sufficiently small to be neglected, for they are smaller than those past aa in the ratio of the conductivities of water and a 0.25-per-cent, solution of sodium chloride. To restore neutrality to this region at the end of the experiment, equivalents of OH' must be added in amount equal to the sum of these two quantities. The quantity (1) represents the OH' ions required to neutralise the H' ions which have arrived; the quantity (2), the deficiency of OH' ions which must be made up.

Since for the titration 0.001 N caustic soda was used, the sum of (1) and (2) must be multiplied by 10⁶ to give the number of cubic centimetres required. The titration should be

$$10^{6}(10^{8} \times 10^{-1}^{+} \times tvae + 10^{3} \times 10^{-14\cdot14 + P_{H}^{+}} t \times \frac{18}{33} vae).$$
 (3)

Inserting the following values

$$P_{\rm H}^{+} = 7.07,$$

 $t = 18,000 \text{ seconds},$
 $v = 33 \times 10^{-4},$
 $ae = 2.93,$

* The determination of the value of the product as, which depends on the voltage applied to the ends of the "side tubes" and upon their shape, was the object of a

the calculated value is 0.027 c.c. 0.001 N caustic soda. Expression (3) is also the expression for the volume of 0.001 N hydrochloric acid required to neutralise the alkali liberated in the region of change of reaction on the right-hand side of the apparatus. So that this titration also should be 0.027 c.c. if the assumptions made are correct. The quantities of acid and alkali found (0.15 and 0.08 c.c. of 0.001 N solution respectively), though of the same order of magnitude as those calculated, are in excess of those quantities anticipated on these suppositions, if the accuracy of these titrations can be trusted. To establish certainty that the difference between the calculated and observed values is significant would require special apparatus, water of exceptional purity, and an expenditure of time which seems scarcely justifiable.

In view of the inaccuracy of the titration of these small quantities nothing can be gained by discussion of possible reasons for the lack of agreement between the calculated and observed values, though it may be remarked that the purer the water used the sharper, smaller, and more nearly equal were the titrations observed.

On the basis of the explanation offered, therefore, the quantities of acid and alkali liberated in a typical Hermann experiment have been predicted, and found in practice, to be of the order 0.03 c.c. of 0.001 N solution. This quantity, though detectable, could not be measured with accuracy.

It may be stated, in conclusion, that invariably when an electric current passes from one aqueous solution to another of different specific conductivity, there will be either acid or alkali liberated at the boundary, depending on the direction of the current. It is widely recognised that in such circumstances a concentration of one of the ions of the feebly conducting solution

separate experiment. It is equal to E/k, where E is the potential difference between the ends of the "side tube" space, and k is their "resistance capacity." For, if the "side tubes" are filled with fluid of specific conductivity s, the current passing may be written aes = Es/k. By "side tubes" are meant the whole of the volume which is not stippled in diagram. The apparatus was filled in the usual manner with normal NaCl and saturated CuSO₄, as electrode fluids, normal NaCl as "middle fluid," and with 0.01 N KCl in the "side tubes." With 115 volts between the electrodes the current passed was 3.58 milliampères. Filling the apparatus in exactly the same way, except that 0.10 N KCl was placed in the side tubes, the current passed was 31 milliampères at the same voltage. If the resistance of the electrode fluids and the normal sedium chloride in the "middle tube," which is common to both, be written ω and the standard values of the specific conductivity of the KCl solutions be taken—

$$\omega + \frac{k}{12 \cdot 3 \times 10^{-4}} = \frac{115}{3 \cdot 58 \times 10^{-3}} : \omega + \frac{k}{11 \cdot 2 \times 10^{-3}} = \frac{115}{31 \times 10^{-3}},$$

from which equations k = 39.2. Hence

$$ae = \frac{\mathbf{E}}{k} = \frac{115}{392} = 2.93.$$

at the boundary will occur: but that H or OH ions will always be found concentrated there, too, has escaped recognition.

A simple experiment can be devised to demonstrate these facts in a striking manner. The apparatus is filled, say, for the experiment under the heading 6th Series, except that, before filling, a little dry azolitmin is dissolved in the middle fluid, and, in such quantities as to produce the same tint, into the side tube fluid as well. Shortly after turning on the current, the litmus will begin to collect at boundaries 1 and 3, and to move away from boundaries 2 and 4. A space above the left-hand tap 1 or 2 mm. deep will be left perfectly clearly defined and colourless in a quarter to half-anhour. Moreover, though this requires care in the amount of azolitmin used, the changes of colour of the litmus at the boundaries demonstrate, in addition, that at each boundary either H or OH' ions concentrate there too. The red litmus anions in the middle tube will not move at all or show any change in their even distribution indefinitely.

The analogy between the acid and alkali liberation at the boundaries of solutions of unequal conductivity (taken together with the supposed bleaching action of litmus in the regions becoming colourless in the experiment just described) led Hermann to consider the phenomena at these boundaries similar to those at metallic electrodes. He attributed them to the discharge of ions. In many experiments with potassium iodide, where, after the experiment, the boundary was tested with starch, and silver nitrate, where metallic silver was looked for, no evidence of this occurring could be found.

Summary.

At the boundary between two solutions of unequal specific conductivity a change of reaction is developed if a difference of potential be maintained between them. Alkali is liberated if the current passes from the better conducting solution to that not conducting so well: acid, if the current passes in the opposite direction. The amounts may be calculated from the potential gradients in the solutions on each side of the boundary, the time for which the difference of potential is maintained, the resistance constant of the vessel employed, the dissociation constant of water, and the known migration velocities of hydrogen and hydroxyl ions.

The Diffusion of Hydrogen through Palladium. By ALERED HOLT, M.A., D.Sc.

(Communicated by G. T. Beilby, F.R.S. Received June 25, 1914.)

(From the Muspratt Laboratory of Physical and Electro-Chemistry, University of Liverpool.)

The diffusion of gases through metallic septa has been the subject of much investigation, for by examining the change in the rate at which the gas diffuses with varying pressures the physical condition of the intrametallic gas has been deduced.

In this field of research hydrogen-palladium has probably received the closest attention, and as the same conclusions have not always resulted from the experimental evidence, little excuse is necessary in presenting new data. Schmidt,* who determined the rate of diffusion between 150° C. and 300° C., and for various pressures, concluded that while the temperature curve is probably quadratic, the pressure curve for the higher pressures may be linear, results which have been questioned by Richardson,† since the experimental data when applied to this latter author's formula for rates of diffusion gave indecisive results.

Winkelmann; had previously expressed the view that the dissociation of the hydrogen molecules was necessary to explain the observed phenomena of diffusion, a contention considered unnecessary by Schmidt, though by assuming it Richardson calculated the heat of dissociation of one gramme-molecule of hydrogen from Schmidt's experimental results, and Winkelmann has since reaffirmed his original conclusion.

Previous to these authors Ramsay|| had made the interesting observation that hydrogen diffusing through palladium into an atmosphere of an indifferent gas never diffused till its partial pressure on the two sides was equal. The pressure was, finally, always greater on the side from which the gas entered the metal.

Recently the present writer, in conjunction with Edgar and Firth, I has shown that, while the rate of diffusion becomes more rapid with rise of temperature, any particular temperature is not characterised by any definite rate of diffusion. The rate depends on what we have called the "activity"

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* 'Ann. Physik' (iv), vol. 13, p. 747.
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^{† &#}x27;Camb. Phil. Soc. Proc.,' vol. 13, p. 27 (1905).

^{† &#}x27;Ann. Physik,' vol. 6, p. 104 (1901).

^{§ &#}x27;Ann. Physik,' vol. 16, p. 773 (1905).

^{|| &#}x27;Phil. Mag.,' vol. 38, p. 206 (1894).

^{¶ &#}x27;Zeit, Phys. Chem.,' vol. 82, p. 513 (1913).

of the metal, i.c. its power of rapid occlusion of gas, and the greater the activity the greater the rate of diffusion. The apparatus and method employed in the following experiments need not be figured or described in detail, since it was essentially the same as that already illustrated,* but a few general remarks may not be out of place.

The experiments group themselves under three heads as follows, and except in two cases represented a temperature range of 130° C. to 300° C.

(1) Measurement of the rate of diffusion from a constant pressure into a vacuum, (2) measurement of the rate of diminution of pressure into a maintained vacuum, and (3) measurement of the rate of diminution of pressure on one side, and increase of pressure on the other side, of a palladium septum during the diffusion of a definite volume of hydrogen.

The actual volume of gas diffusing through the heated metal was not determined, only the variation of pressure with time being recorded, the rate being taken to be the number of seconds required for a change in pressure of 1 mm. At the temperatures of the experiments palladium becomes saturated with hydrogen very rapidly, and hence it was only necessary to wait a few minutes after the commencement of each experiment before readings could be begun. It was found that in every experiment a graph in which the logarithms of decreasing pressures were plotted against time yielded with considerable exactness two straight lines cutting one another at some definite point. In the case of increasing pressures the graph of the logarithms of atmospheric pressure (760 mm.) minus the observed increasing pressure gave two straight lines when plotted against time.

These graphs for a series of experiments are illustrated in the figure; they represent the experimental data given in the Tables later in this paper.

The relation may therefore be expressed:-

$$\frac{1}{t}\log\frac{p_1}{p_2} = K \text{ for decreasing pressure,}$$

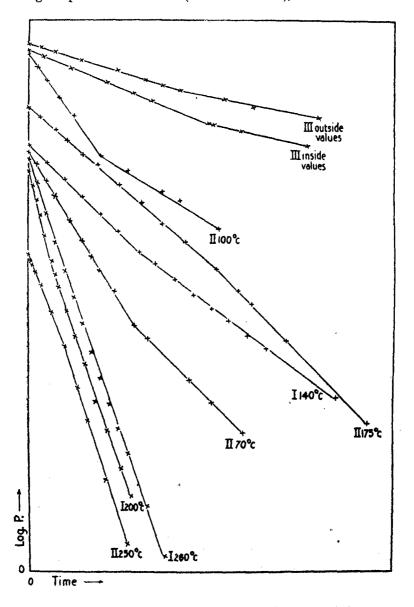
and

$$\frac{1}{t}\log\frac{760-p_1}{760-p_2} = K \text{ for increasing pressure.}$$

From these relations it is apparent that the gas is diffusing through the metal at a rate proportional to the pressure, not to the square root of the pressure, and hence according to the partition law the intramolecular gas is in a simple molecular condition.

It is, however, doubtful whether such a conclusion as to the molecular state of the gas is justified, for the occlusion of hydrogen by palladium is a far from simple phenomenon.

It has already been mentioned that the value of K calculated from either of the above expressions does not usually remain a constant throughout the whole range of pressures examined (100 to 700 mm.), but has two different



values, one for the initial and the other for the final portion of the rate curve. Reference to the graphs above will show, however, that though the rate curve can be closely represented by two equations of either of the above types

giving different values of K and exhibiting a definite point of transition from one value to the other, this can only be an approximation, for the phenomenon of diffusion is perfectly continuous. Further, it does not hold for pressures lower than about 90 mm., where the rate begins to diminish rapidly, and does not appear to be proportional to any definite function of the pressure.

In a recently published paper,* the author has shown that the rate of solution of hydrogen at constant pressure by palladium foil cannot be represented by a simple expression since there is a discontinuity, in the rate curve, which consists of two portions of the same general curvature. The peculiar form of these rate curves has been attributed to two modifications of the metal, differing solely in the packing of the particles. The discontinuity of the value of K in the present experiments on diffusion almost certainly arises from a similar cause, for as the temperature increases the discontinuity becomes less, just as has been observed in the case of the rate of solution. It is unfortunately impossible to measure the rate of diffusion through palladium black to see whether the discontinuity of K ceases, but the close parallelism between the phenomena of solution and diffusion in palladium foil, and the explicability of the former, on the basis of metallic allotropes, points to a similar explanation in the case of the results given in the present communication.

It might be argued from an inspection of the graphs and data given in the following Tables that neither value of K in any given experiment is really a constant, but is continually and slowly altering. This is probably true, and as has been mentioned it is only an approximation to represent the graphs by straight lines, but the variation from the relation

Rate x pressure = constant

is so slight as to be easily explained by the changes of solubility of gas in the metal with pressure.

If at any given temperature we suppose the amount of gas retained by the metal to be the same as that occluded at a pressure equal to the mean value of the pressures on either side of the metallic septum, then as diffusion proceeds this mean pressure will vary, and so will the gas-content of the metal. Since the rate of diffusion has been shown to vary from one experiment to another at the same temperature and to depend on the activity of the metal, it follows that the amount of gas retained and the speed with which it adjusts itself to the ever varying pressure must have some slight influence on the rate of diffusion.

At temperatures over about 120° C., the change in the solubility of

^{* &#}x27;Roy. Soc. Proc.,' A, vol. 90, p. 226 (1914).

hydrogen in palladium between 380 mm. and 710 mm., or 380 mm. and 50 mm. (the mean values of the pressures on the two sides at the beginning and end of an experiment) is not great, and hence there is no pronounced variation between the experimentally determined points and the straight lines of the graph.

The following Tables contain data of a few of the many experiments carried out. The pressure readings in brackets () were not determined experimentally, but were read off the graphs as the intersection point of the two straight lines. Series I gives examples of the rates of diffusion into a vacuum from constantly maintained atmospheric pressure. Series II represents the rate of diminution of pressure into a maintained vacuum, while Series III shows the rate of diminution of pressures on one side and the corresponding rise of pressure on the other.

The figures in heavy type show the pressures at which the second value of K begins. They represent the intersection of the straight lines on the graph, or, what is the same thing, the pressure at which the values of

$$\frac{1}{t_2 - t_1} \log \frac{p_1}{p_2} = \mathbf{K}$$

show marked variation.

Conclusion.

Between 700 mm. and 100 mm. pressure hydrogen appears to diffuse through palladium heated to about 100° C. to 300° C. at a rate proportional to the pressure of the gas, though the rate curve appears to consist of two portions. It is shown that by assuming the pressure-time curve to consist of two exponentials of different slope, the experimental values can be reproduced with considerable accuracy, certainly with an accuracy which leaves no question as to the proportionality of the rate to the pressure, not to the square root or any other power of the pressure.

As in the case of the rate of solution of hydrogen at constant pressure by palladium foil where discontinuous curves are obtained, the two exponentials of different slope are accounted for by metallic allotropes.

At pressures lower than 100 mm. the rate of diffusion becomes more and more slow, and is not apparently related to any simple function of the pressure.

Temperature, 140° C.	jre, 140	y C.			Temp	Temperature, 200° C.	<i>رد</i> د.		Tem	Temperature, 200° C.	r C
me.				Time.	ون			Time.	ne.		
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Dr. A. Holt.

Series II.

T	ime.		K	T	ime.		K	
Observed.	Calculated from mean value of K.	Pressure observed.	$\left(\frac{1}{\ell}\log \frac{p_1}{p_2}\right).$	Observed.	Calculated from mean value of K.	Pressure observed.	$\left(\frac{1}{t}\log\frac{p}{p}\right)$	21).
	Temperate	ure, 70° C) .		Temperatu	re, 175° C).	
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	5 9 ·1	(211)		87	88 •2	315	0.0042	
66	66 •1	195	0 ·0049 \$	104	106.2	265	0.0051	
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101	102 .0	180	0.0049	123	125 ·8	212	0 .0052	۱ ۱
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74	74 ·1	800	0.0029	88	82 .7	248	0.0157	1
84	88 .4	282	3	48	42 .8	172	0.0167	إ
105	108 ·8	288	0 0031	54	58 .7	116	0.0101	7 2

Series III.—Temperature, 140° C.

T	ime.		ĸ	,	T	ime.		к	
Observed.	Calculated from mean values of K.	Pressure observed.	$\left(\frac{1}{t}\log \frac{p}{p}\right)$	<u>1</u>).	Observed.	Calculated from mean values of K.	Pressure observed.	$\left(\frac{1}{t}\log\frac{760}{760}\right)$	$\left(\frac{p-p_1}{p-p_2}\right)$
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min.	min.	mm.		1	min.	min.	mm.		
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Approximately Permanent Electronic Orbits and the Origin of Spectral Series.

By George W. Walker, A.R.C.Sc., M.A., F.R.S., formerly Fellow of Trinity College, Cambridge.

(Received October 30, 1914.)

The electrodynamical theory which we owe to Lorentz and Larmor provides theoretically a logical and consistent scheme whereby the equations of motion of electronic systems may be formulated. But, unfortunately, even most simple cases lead to equations of such complexity that the attempt to deduce exact solutions must at present be abandoned since there is no mathematical machinery available for the purpose. We have accordingly to make some simplifying assumptions, not strictly true, in order to obtain an approximate solution. In many cases, results are thus obtained which give a very close agreement with observation, and this is so far gratifying. But modern experimental work in radiation makes it clear that the phenomena have not yet been co-ordinated with the electrodynamical theory of electrons.

It is reasonable to enquire if this is due to the failure of mathematicians to provide an explanation, whether because the approximations used are not accurate enough, or because the conception of the electronic systems considered is not sufficiently general?

As indicating failure due to the use of approximate equations, it may be pointed out that the neglect of radiation terms, or even their treatment by an approximation due to Larmor and Lorentz (valid in certain cases) is attended with considerable danger, and in former papers to the Royal Society I have given cases in which such approximate treatment would give a quite inadequate notion of the effects to be expected.

As regards the specification of an electronic system, it is remarkable that so many calculations take account of electrostatic forces only. In any attempt to deal with the phenomena of spectra it seems obvious that only a theory which takes account of magnetic and electromagnetic forces is likely to meet with success.

Hicks has on several occasions insisted on this, and recently* he has given an illustration showing how large the effect of internal magnetic force may be in affecting the motion of an electron.

Conway+ has outlined a theory of spectral series, which appears to me most

^{* &#}x27;Proc. Roy. Soc.,' vol. 90, p. 856 (1914).

^{† &#}x27;Phil. Mag.,' vol. 26, p. 1010 (1913).

important. My investigations show that some vital modifications have to be introduced, and that we then get results of a very promising character in the explanation of series in accordance with pure electrodynamics.

A single electron carries a definite electric charge (whether of positive or negative sign) as a primary part of its constitution. It is also supposed to have a definite radius. Such an electron is capable of internal rotation as well as of translation, but comparatively little study has been made as to the consequences of rotation. It implies, of course, a magnetic moment, and some would thereby hope to explain magnetisation. I confess that I have no logical ground for sharing that hope, rather the reverse; and at present it seems necessary to retain a true permanent magnetic moment, as part of the constitution of an electron. We need not on that account omit the possibility of magnetic moment arising from rotation of the electron. It must, in fact, exist, although subject to variation of amount.

The complete formulation of the equations of motion of two such nuclei might be made, but it is a formidable undertaking. I accordingly take a more limited problem. Although it is thus only an illustration, the results are worthy of attention; and it may, like the artificial problem of a particle moving round a fixed centre of force, serve as a guide to real cases.

Corresponding to the atom, which is supposed to be comparatively massive, we shall take a nucleus of radius a, with a positive charge E, and a permanent magnetic moment μ . It is constrained to be fixed both as regards translation and rotation. The motion we propose to examine is that of a particle corresponding to a corpuscle with a negative charge -e. We shall assume that it has no permanent internal magnetic moment and that internal rotation is neglected. The speed of the particle is to be small enough to admit the use of its invariable mass m.

It will conduce to clearness if we begin by finding the motion which is possible when the radiation is neglected. Take the origin of co-ordinates at the centre of the positive nucleus and the z axis along the axis of magnetic moment. Further, let r, θ , ϕ be the polar co-ordinates of the moving corpuscle, and C the velocity of light.

On account of the electric and magnetic forces the motion is characterised by a Lagrangian function L, where

$$\frac{L}{m} = \frac{1}{2} (r^2 + r^2 \dot{\theta}^2 + r^2 \sin^2 \theta \dot{\phi}^2) + \frac{e\mu}{mr} \sin^2 \theta \dot{\phi} + \frac{eEC^2}{mr},$$

when the corpuscle is outside the nucleus, from which we deduce an energy integral,

$$\frac{1}{2}(r^2 + r^2\dot{\theta}^2 + r^2\sin^2\theta\dot{\phi}^2) - \frac{eEC^2}{mr} = \frac{1}{2}v^2$$
 (a constant),

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and an integral of angular momentum,

$$r^2 \sin^2 \theta \dot{\phi} + \frac{e\mu}{mr} \sin^2 \theta = h$$
 (a constant).

The equations of motion, which we require to ascertain if orbits are stable are

$$\ddot{r} - r \sin^2 \theta \dot{\phi}^2 - r \dot{\theta}^2 + \frac{e\mu}{mr^2} \sin^2 \theta \dot{\phi} + \frac{eEC^2}{mr^2} = 0.$$

$$\frac{d}{dt} r^2 \dot{\theta} - r^2 \sin \theta \cos \theta \dot{\phi}^2 - 2 \frac{e\mu}{mr} \sin \theta \cos \theta \dot{\phi} = 0,$$

$$\frac{d}{dt} \left\{ r^2 \sin^2 \theta \dot{\phi} + \frac{e\mu}{mr} \sin^2 \theta \right\} = 0.$$

The equations show that there may be steady motions in circular orbits. If, therefore, we assume

$$r=r_0, \quad \theta=\alpha, \quad \dot{\phi}=\omega,$$

for the constant values, we get, provided $\alpha \neq \frac{1}{2}\pi$,

$$\omega + \frac{2e\mu}{mr_0^3} = 0,$$
 $\omega^2 - \frac{e\mu\omega}{mr_0^3} = \frac{eEC^2}{mr_0^3 \sin^2\alpha}.$

$$r_0^3 = -2\frac{e\mu}{m\omega}, \quad \sin^2\alpha = -\frac{1}{8}\frac{EC^2}{\mu\omega}.$$

Hence

Thus such orbits exist provided ω is negative and numerically greater than $\frac{1}{3} EC^2/\mu$, and if, further, r_0 is greater than a, the radius of the nucleus. This requires that $\frac{1}{6} mEC^2\alpha^3/e\mu^2$ should be less than 1.

A disturbance from a steady state may be examined in the usual way by assuming that r, θ , ϕ , differ from their steady values by small quantities proportional to $e^{i\lambda t}$.

We find that

$$\lambda^{2} = \frac{1}{2} \omega^{2} \left[(1 + \frac{9}{4} \sin^{2} \alpha) \pm \left\{ (1 + \frac{9}{4} \sin^{2} \alpha)^{2} - 3 \sin^{2} 2 \alpha \right\}^{\frac{1}{2}} \right]$$

$$\equiv \frac{1}{2} \omega^{2} \left[(1 + \frac{9}{4} \sin^{2} \alpha) + \left\{ (1 - \frac{1}{4} \sin^{2} \alpha)^{2} + 3 \sin^{4} \alpha \right\}^{\frac{1}{2}} \right].$$

Both values of λ^2 are positive, so that if the orbits exist they are stable.

When $\alpha = \frac{1}{2}\pi$ the equation is

$$\omega^2 - \frac{e\mu\omega}{mr_0{}^3} = \frac{e\mathrm{EC}^2}{mr_0{}^3}$$
, or $r_0{}^3 = \frac{e}{m} \cdot \frac{(\mathrm{EC}^2 + \mu\omega)}{\omega^2}$.

For displacements in the plane of the orbit varying as $e^{i\lambda t}$ we get

$$\lambda^2 = \frac{\omega^2 \left\{ \text{EC}^2 + \left(\sqrt{3-1}\right)\mu\omega \right\} \left\{ \text{EC}^2 - \left(\sqrt{3+1}\right)\mu\omega \right\}}{\left(\text{EC}^2 + \mu\omega \right)^2},$$

so that for stability this must be positive.

For displacements perpendicular to the plane of the orbit varying as $e^{i\lambda t}$ we get

$$\lambda^{2} = \omega^{2} \frac{(EC^{2} + \mu\omega)(EC^{2} + 3\mu\omega)}{(EC^{2} + \mu\omega)^{2}},$$

and for stability this must be positive.

Hence with ω positive the orbits are entirely stable, with r_0 ranging from $a \left\{ (3\sqrt{3}+5) \frac{e\mu^2}{m \text{EC}^2 a^3} \right\}^{\frac{1}{5}}$ to ∞ , provided $\frac{m \text{EC}^2 a^3}{e\mu^2} < (3\sqrt{3}+5)$. If this condition is not satisfied, r_0 ranges from a to ∞ .

With ω negative, the orbits are entirely stable with r_0 ranging from $a\left(\frac{6e\mu^2}{mEC^2\alpha^3}\right)^{\frac{1}{2}}$ to ∞ , provided $\frac{mEC^2\alpha^3}{e\mu^2} < 6$. If this condition is not satisfied, r_0 ranges from a to ∞ .

So far we have assumed that the corpuscle does not penetrate within the nucleus of radius a. If it does, the equations change form, and we must make a further specification as to the interior. A usual hypothesis is that the charge is uniformly distributed throughout the sphere. I shall follow Conway in this supposition and further assume that the magnetic moment is uniformly distributed; but in anticipation of an important point which will occur later, I shall suppose that the dielectric ratio of the matter inside is given by K, where $K^{\frac{1}{2}} = C/C'$.

In order to secure proper continuity with the equations outside the nucleus we find that the equations inside are:—

$$\begin{split} \ddot{r} - r \sin^2 \theta \dot{\phi}^2 - r \dot{\theta}^2 - \frac{e\mu}{ma^5} r \left(5a^2 - 6r^2 \right) \sin^2 \theta \dot{\phi} + \frac{eEC'^2}{ma^3} r &= 0. \\ \frac{d}{dt} r^2 \dot{\theta} - r^2 \sin \theta \cos \theta \dot{\phi}^2 - \frac{e\mu}{ma^5} r^2 \left(5a^2 - 3r^2 \right) \sin \theta \cos \theta \dot{\phi} &= 0. \\ \frac{d}{dt} \left\{ r^2 \sin^2 \theta \dot{\phi} + \frac{1}{2} \frac{e\mu}{ma^5} r^2 \left(5a^2 - 3r^2 \right) \sin^2 \theta \right\} &= 0. \end{split}$$

There is a Lagrangian function,

$$L = \frac{1}{2} \left\{ \dot{r}^2 + r^2 \dot{\theta}^2 + r^2 \sin^2 \theta \dot{\phi}^2 \right\} + \frac{1}{2} \frac{e\mu}{m\mu^5} r^2 (5a^2 - 3r^2) \sin^2 \theta \dot{\phi} - \frac{1}{2} \frac{eEC^2}{m\mu^3} r^2,$$

from which we can deduce an energy integral and an integral of angular momentum.

There are steady circular orbits given by

$$t = r_0, \quad \theta = \alpha, \quad \dot{\phi} = \omega;$$

and if $\alpha \neq \frac{1}{2}\pi$ we get

$$\omega^{2} + \frac{e\mu}{ma^{5}} \omega \left(5 a^{2} - 6 r_{0}^{2}\right) = \frac{eEC'^{2}}{ma^{3} \sin^{2} \alpha},$$

$$\omega + \frac{e\mu}{ma^{5}} \left(5 a^{2} - 3 r_{0}^{2}\right) = 0.$$

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Thence

$$\omega r_0^2 \sin^2 \alpha = -\frac{1}{3} \frac{EC'^2 a^2}{\mu}$$
.

Thus, as Conway points out, all such orbits if they exist have the same angular momentum.

For disturbance varying as $e^{i\lambda t}$ we get

$$\lambda^2 = \omega^2 \cos^2 \alpha + \left(\frac{e\mu}{ma^5}\right)^2 \sin^2 \alpha (6r_0^2 - 5a^2)^2$$
 and $\lambda^2 = 0$,

so that the orbits are stable as regards one type of disturbance and neutral as regards the other.

The relation between r_0 and α is

$$\sin^2\alpha = \frac{1}{9} \cdot \frac{m E C'^2 a^3}{c \mu^2} \cdot \frac{1}{\{25/36 - (5/6 - r_0^2/a^2)^2\}}.$$

As r_0 ranges from a to $\left(\frac{5}{6}\right)^{\frac{1}{2}}a$, $\sin^2\alpha$ ranges from $\frac{4}{24} \cdot \frac{mEC'^2a^3}{e\mu^2}$ to $\frac{4}{25} \cdot \frac{mEC'^2a^3}{e\mu^2}$.

 $\sin^2 \alpha$ then increases to 1,

while
$$r_0$$
 decorates from $\left(\frac{5}{6}\right)^{\!\!\!4}a$ to $\left[\frac{1}{6}\left\{5-\left(25-4\,\frac{m\mathrm{EC}'^2a^3}{e\mu^2}\right)^{\!\!\!4}\right\}\right]^{\!\!\!4}$.

Clearly the orbits are possible only if $\frac{4}{25}$. $\frac{mEC'^2a^3}{e\mu^2} < 1$,

When $\alpha = \frac{1}{2}\pi$ we get the condition

$$\omega^2 + \frac{e\mu}{ma^5} \omega (5a^2 - 6r_0^2) = \frac{eEC'^2}{ma^3}$$

or

$$\frac{r_0^2}{a^2} = \frac{5}{6} + \frac{1}{6} \cdot \frac{\omega^2 - eEC'^2/ma^3}{\omega e\mu/ma^3}.$$

For disturbance in the plane varying as $e^{i\lambda t}$ we get

$$\lambda^2 = 4\omega \left\{ \omega + \frac{e\mu}{ma^3} \left(5 - 3 \frac{r_0^2}{a^2} \right) \right\} + \left(\frac{e\mu}{ma^3} \right)^2 \left(5 - 6 \frac{r^2}{a^2} \right)^2.$$

For disturbance perpendicular to the plane

$$\lambda^{2} = \omega \left\{ \omega + \frac{e\mu}{ma^{2}} \left(5 - 3 \frac{r_{0}^{2}}{a^{2}} \right) \right\}.$$

Thus stability is secured if the latter quantity is positive. The possible range is as follows:—

$$r_{0} = a...... \qquad \omega \text{ is positive and } = \frac{1}{2} \cdot \frac{e\mu}{ma^{3}} + \left\{ \left(\frac{1}{2} \cdot \frac{e\mu}{ma^{3}} \right)^{2} + \frac{eEC'^{2}}{ma^{3}} \right\}^{\frac{1}{2}},$$

$$r_{0} = \left(\frac{5}{6} \right)^{\frac{1}{2}} a ... \qquad \omega \qquad , \qquad = \left(\frac{eEC'^{2}}{ma^{3}} \right)^{\frac{1}{2}},$$

$$r_{0} = 0..... \qquad \omega \qquad , \qquad , \qquad = -\frac{5}{2} \cdot \frac{e\mu}{ma^{3}} + \left\{ \left(\frac{5}{2} \cdot \frac{e\mu}{ma^{3}} \right)^{2} + \frac{eEC'^{2}}{ma^{3}} \right\}^{\frac{1}{2}},$$

$$r_0 = 0 \dots \qquad \omega \text{ is negative and } = -\frac{5}{2} \cdot \frac{e\mu}{ma^3} - \left\{ \left(\frac{5}{2} \cdot \frac{e\mu}{ma^3} \right)^2 + \frac{eEC'^2}{ma^3} \right\}^{\frac{1}{3}},$$

$$r_0 = \left(\frac{5}{6} \right)^{\frac{1}{6}} a \quad \dots \quad \omega \qquad , \qquad , \qquad = -\left(\frac{eEC'^2}{ma^3} \right)^{\frac{1}{3}},$$

$$r_0 = a \dots \qquad \omega \qquad , \qquad , \qquad = \frac{1}{2} \cdot \frac{e\mu}{ma^3} - \left\{ \left(\frac{1}{2} \cdot \frac{e\mu}{ma_3} \right)^2 + \frac{eEC'^2}{ma^3} \right\}^{\frac{1}{3}}.$$

For positive values of ω the orbits are stable since $r_0 < a_n'$ while for negative values of ω we must exclude the range for which ω lies between -

$$-\frac{5}{2} \cdot \frac{e\mu}{ma^3} + \left\{ \left(\frac{5}{2} \cdot \frac{c\mu}{ma^3} \right)^2 - \frac{e\mathbf{E}\mathbf{C}'^2}{ma^3} \right\}^{\frac{1}{2}}$$
$$-\frac{5}{2} \cdot \frac{e\mu}{ma^3} - \left\{ \left(\frac{5}{2} \cdot \frac{e\mu}{ma^3} \right)^2 - \frac{e\mathbf{E}\mathbf{C}'^2}{ma^3} \right\}^{\frac{1}{2}}.$$

and

These results may usefully be made more general by assuming that the total magnetic moment μ consists of two parts, μ_1 and μ_2 , where $\mu_1 + \mu_2 = \mu$. If the part μ_1 is uniformly disturbed throughout as before, while μ_2 is confined to the surface, the effect of the latter is to superpose a uniform field within the nucleus. The equations for the circular orbits of equal angular momentum are now

$$-\omega = \frac{5e\mu_1}{ma^3} - \frac{e\mu_2}{ma^3} - \frac{3e\mu_1}{ma^3} \cdot \frac{r_0^2}{a^2}.$$
$$\omega r_0^2 \sin^2 \alpha = -\frac{1}{3} \cdot \frac{EC'^2 a^2}{\mu_1}.$$

The general character of the orbits is not altered, but the necessity for this subdivision will become apparent when we attempt to fit our final results with observation.

It will now be convenient to consider the magnitude of the quantities involved, and for the moment it will suffice to take the order of magnitude only without entering on precise numerical estimates.

Thus let us take $E = e = 10^{-20}$, $e/m = 10^7$, $\mu = 10^{-21}$, $a = 10^{-8}$, $C^2 = 10^{21}$.

The quantity $\frac{mEC^2a^3}{e\mu^2}$ is thus of order 10^{12} ,

$$\left(\frac{eEC^2}{ma^3}\right)^{\frac{1}{6}} \qquad \qquad 10^{16},$$

$$\frac{e\mu}{ma^3} \qquad \qquad \qquad 10^{10}.$$

Thus, if K is unity, it is clear that the stationary orbits with constant angular momentum discovered by Conway cannot exist for the given system, and although the equatorial orbits do exist, it will be noted that

the frequency varies so little within the nucleus that the explanation of series on these lines would fail,

It would hardly be considered expedient to suppose that μ is any large multiple of the above value, and the alternative course of reducing α to a small enough value (of order 10^{-12}) to make the orbits possible, carries with it, as a consequence, that the angular momentum in the orbits is but a small fraction of the value known as Planck's unit. Nevertheless, the theory outlined by Conway gives such good promise that a method of escape from the difficulty just raised is worthy of consideration.

We may suppose that the charge of the nucleus is not uniformly distributed, but is chiefly concentrated near the surface. This hypothesis, or, as an alternative, the hypothesis that the material has a large value of K, would enormously reduce the electrostatic forces inside the nucleus and so make the orbits possible. We can still obtain frequencies of the proper order, and, moreover, now with a suitable range by taking a of order 10^{-10} . But it must be carefully noted that the angular momentum now has a value very small compared with Planck's value. As already stated, I think we are required to retain the view that the magnetic moment of the nucleus is permanent and does not arise from rotation. It is also desirable and permissible to retain 10^{-8} as the effective radius for external purposes, and to regard 10^{-10} as the radius of the region within which the orbits are possible, whether as a consequence of small electrical density or of a large value of K.

The form of the meridian section of the surface on which the particles with the same angular momentum lie is of interest. Taking the simpler case in which μ is undivided, the curve consists of two branches with a cusp at $r_0 = (\frac{\pi}{6})^{\frac{1}{2}} a$. If $\frac{4}{26} (mEC'^2 a^3/e\mu^2)$ is just a little less than unity, the orbits are rather close to the equatorial plane and within a narrow range $r_0 = 0.9a$ to a. The values of ω , which are negative, range from two to two and a half times $e\mu/ma^3$, which is hardly enough. On the other hand, if $\frac{4}{\sqrt{5}}(mEC'^2a^3/e\mu^2)$ is small the orbits lie rather close to the magnetic axis of the nucleus and range from $r_0 = 0$ to α while ω ranges from two to five times $e\mu/m\alpha^3$, which is more suitable. The frequency of a disturbance is not in general $\omega/2\pi$, but on the latter assumption the difference is small. Anticipating a result which will appear, when we take account of the radiation, that only for certain series of values of r_0/a are the orbits approximately permanent, we get a promising explanation of certain spectral series. But there is one weakness. For a given value of r_0 there is but one frequency of disturbance. Thus the series of lines can have no structure, although they probably have general diffuseness.

The equatorial orbits, although they have not all the same angular momentum, may supply the deficiency. Corresponding to a given value of r_0 there are two values of ω , and, within certain ranges, both are stable. Further, for each value of ω there are two frequencies of disturbance. Thus the series may be expected to give fourfold structure. The formulæ in this case cannot, in general, be put in the simple form which obtains for the orbits of same angular momentum, and which agrees so closely with the empirical formulæ. Within certain limits, however, approximate formulæ of the empirical type would be valid.

We now proceed to consider the effects to be expected on account of radiation from the particle. Since it moves in a region of electric and magnetic force in phase with its own, the usual assumption that it radiates proportionally to the square of its resultant acceleration is not applicable. The forces arising from the radiation going on both inside and outside the nucleus entirely modify the problem. It appears that certain of the stationary orbits are picked out in series as having definite frequencies, and for these the radiation is comparatively small. These orbits may then continue to exist for a long time (optically), and so manifest their existence in the spectrum. The intermediate orbits are not permanent and the radiation is considerable. They must, however, take part in the process by which the radiation from the more permanent orbits is maintained, and some portion of their radiation will be exhibited outside the nucleus as Röntgen radiation of short wave-length (determined by the outer radius of the nucleus).

These results may be deduced from the fundamental equations.

It may be recalled that Lamb* investigated the behaviour of a fixed sphere of atomic dimensions $a = 10^{-8}$ with a large dielectric ratio. He shows that series of vibrations of optical frequencies may arise and that the damping is very slight. Although Lamb's series are not in agreement with the empirical formulæ for observed series, I have for some time entertained the view that some simple modification of the vibrating system would give the empirical forms. In 'Phil. Trans.,' 1910, I obtained extensions of Lamb's equations and showed that, in addition to the optical vibrations, there was one rapidly damped vibration of wave-length comparable with the circumference of the sphere $2\pi 10^{-8}$. When the paper was written we had no knowledge of the wave-length of Röntgen radiation, but it is known now that it is of this order.

Returning, now, to the problem before us, the motion of the particle will set up radiation both inside and outside the nucleus. That radiation, as well

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as the exciting radiation, can be represented in terms of disturbances of electric and magnetic type, arising from harmonics of different orders. These produce reactions on the moving particle. Complete formulation might be made but is hardly yet justified. It will be simpler and clearer to confine attention to the first-order terms.

Take first the first-order disturbance of electric type with axis along the magnetic axis of the nucleus. The expressions for the electric and magnetic force inside are (loc. cit. ante, p. 174)—

$$\begin{split} (X, Y, Z) &= \frac{C'}{r^3} (0, 0, -1) \left\{ r^2 (\psi_1'' + \psi_2'') + r (\psi_1' - \psi_2') + \psi_1 + \psi_2 \right\} \\ &+ \frac{C'z}{r^5} (x, y, z) \left\{ r^2 (\psi_1'' + \psi_2'') + 3 r (\psi_1' - \psi_2') + 3 (\psi_1 + \psi_2) \right\}. \end{split}$$

$$\mathbf{K}^{-\frac{1}{2}}(\alpha,\beta,\gamma) = \frac{\mathbf{C}'}{r^3}(-y,x,0) \left\{ r (\psi_1'' - \psi_2'') + \psi_1' + \psi_2' \right\},$$

where
$$\psi_1 = \psi_1(C't - r)$$
, $\psi_2 = \psi_2(C't + r)$, and $\psi_1(C't) + \psi_2(C't) = 0$.

Since K is to be taken as very large, the reaction on the particle depends almost entirely on the dynamic force arising from (α, β, γ) on the velocity $(\dot{x}, \dot{y}, \dot{z})$, since the electric force is small in comparison.

Thus the additional terms to be introduced in the equations of motion of the particle vary as $\{r(\psi_1''-\psi_2'')+\psi_1'+\psi_2'\}$. These will vanish and the stationary orbit will be permanent for that type of disturbance if r is selected so that

$$r(\psi_1'' - \psi_2'') + \psi_1 + \psi = 0.$$

Hence, taking $\psi_1 = A e^{iK b_A (C'l-r)/n}$, $\psi_2 = -A e^{iK b_A (C'l+r)/n}$, we get the condition

$$\tan K^{\dagger} \lambda r / a = K^{\dagger} \lambda r / a.$$

The roots are

$$\frac{1}{\pi}$$
 K³ $\lambda r/\alpha = 1.4303$, 2.4590, 3.4709, 4.4774, 5.4818, 6.4844, etc.,

and the higher roots are nearly

$$(n+\frac{1}{2})-\frac{1}{\pi^2}(n+\frac{1}{2})^{-1}$$

In order to satisfy the boundary conditions at the surface of the nucleus, $K^{j}\lambda$ is determined by

$$\tan \mathbf{K}^{\flat}\lambda = \mathbf{K}^{\flat}\lambda \left\{1 - \frac{\mathbf{K}\lambda^{\flat}(1-i\lambda)}{(\mathbf{K}-1)(1-i\lambda)-i\mathbf{K}\lambda^{\flat}}\right\}\,,$$

Since K is large, the real parts of the roots are very nearly those of $\tan K^{\dagger}\lambda = K^{\dagger}\lambda$, while the imaginary parts are very small. There is also the special root $\lambda = \frac{i}{2} \pm \frac{1}{2} \sqrt{3}$.

Thus $\frac{1}{\pi}K^{\dagger}\lambda$ has the values already given for $\frac{1}{\pi}K^{\dagger}\lambda\frac{r}{a}$. Hence r/a may be given series of values, viz.,

$$r/a = 1$$
, $\frac{1\cdot 4303}{2\cdot 4590}$, etc., $\frac{1\cdot 4303}{n+\frac{1}{2}}$, 0;
 $r/a = 1$, $\frac{2\cdot 4590}{3\cdot 4709}$, etc., $\frac{2\cdot 4590}{n+\frac{1}{2}}$, 0;

and so on.

Our argument, then, is that at these distances the corresponding orbits are for optical purposes of considerable permanence for disturbance of this type, and so give rise to series, while intermediate orbits, being soon deranged by this type of disturbance, give no optical effect.

The orbits of equal angular momentum are given by

$$-\omega = -\frac{e\mu_2}{ma^3} + \frac{5e\mu_1}{ma^3} \left(1 - \frac{3r_0^2}{a^2}\right),$$

where $\mu_2 + \mu_1 = \mu$ and r/a may be given the above series of values. Thus, if the conditions are such that the orbits lie close to the axis, the frequencies of the lines in the series are

$$\nu = -\frac{1}{2\pi} \omega = -\frac{1}{2\pi} \cdot \frac{e\mu_2}{ma^3} + \frac{5}{2\pi} \cdot \frac{e\mu_1}{ma_3} \left(1 - \frac{3}{5} \cdot \frac{r_0^2}{a^2}\right).$$

The head is $\nu=\frac{1}{\pi}\cdot\frac{e\mu_1}{ma_3}-\frac{1}{2\pi}\cdot\frac{e\mu_2}{ma_3}$ and the tail is $\nu=\frac{5}{2\pi}\cdot\frac{e\mu_1}{ma^3}-\frac{1}{2\pi}\cdot\frac{e\mu_2}{ma^3}$.

Towards the tail the values will be approximately

$$\nu = -\frac{1}{2\pi} \cdot \frac{e\mu_2}{ma^3} + \frac{5}{2\pi} \cdot \frac{e\mu_1}{ma^3} \left\{ 1 - \frac{\frac{3}{5}S}{(n+\frac{1}{5})^2} \right\},\,$$

where S for the different series has the values

$$(1.4303)^2$$
, $(2.4590)^2$, etc.

Near the head the more exact values must be introduced in place of $(n+\frac{1}{2})^2$. If, however, the orbits approach the equatorial plane, and we consider also equatorial orbits which are not all of the same angular momentum, the formula, although having the same general features, cannot be accurately expressed in so simple a form, and, moreover, limits are set to the possible number of lines.

We next consider the first-order disturbance of magnetic type. The field is given (as at loc. cit. ante, p. 187) by

$$\begin{split} (X,Y,Z) &= \frac{\mathrm{C}'}{r^3}(y,-x,0) \left\{ r \left(\psi_1'' - \psi_2'' \right) + \psi_1' + \psi_2' \right\}, \\ K^{-\frac{1}{2}}(\alpha,\beta,\gamma) &= \frac{\mathrm{C}'}{r^3}(0,0,-1) \left\{ r^3 \left(\psi_1'' + \psi_2'' \right) + r \left(\psi_1' - \psi_2' \right) + \psi_1 + \psi_2 \right\} \\ &+ \frac{\mathrm{C}'z}{r^3}(x,y,z) \left\{ r^3 \left(\psi_1'' + \psi_2'' \right) + 3 r \left(\psi_1' - \psi_2' \right) + 3 \left(\psi_1 + \psi_2 \right) \right\}. \end{split}$$

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As before, the reactions on the particle arise chiefly from α , β , γ , and are found to consist of terms proportional to

$$r(\psi_1' - \psi_2') + \psi_1 + \psi_2$$
$$r^2(\psi_1'' + \psi_2'') + r(\psi_1' - \psi_2') + \psi_1 + \psi_2.$$

and to $r^2 (\psi_1^{"})$. They will vanish only if

$$\tan K^{\frac{1}{2}} \lambda r/a = K^{\frac{1}{2}} \lambda r/a$$
 and $\tan K^{\frac{1}{2}} \lambda r/a = \frac{K^{\frac{1}{2}} \lambda r/a}{1 - K \lambda^{\frac{1}{2}} a^{\frac{1}{2}} / a^{\frac{1}{2}}}$.

We cannot in general satisfy both with the same value of r, but it may be noted that for orbits near the axis it is more important to satisfy the first condition, while for orbits near the equatorial plane the more important condition is the second. We may therefore expect approximately permanent orbits. If they are near the axis we have the series

$$\frac{1}{\pi} K^{\frac{1}{2}} \lambda r / a = 1.4303, \ 2.4590, \ ..., \ n + \frac{1}{2} - \frac{1}{\pi^2} (n + \frac{1}{2})^{-1},$$

while, if they are near the equatorial plane, we have

$$\frac{1}{\pi} K^{\dagger} \lambda r / a = 0.87334, 1.9470, ..., n - \frac{1}{\pi^3} n^{-1}$$

In either case the values of Kia are determined by the equation

$$\tan K^{\dagger}\lambda = \frac{K^{\dagger}\lambda}{1 - K(1 - i\lambda)},$$

and, since K is large, the roots are practically

$$\frac{1}{\pi} K^{2} \lambda = 1, 2, 3, ..., n,$$

while the imaginary part is small.

There is the special root $\lambda = i$ which corresponds to a rapidly damped disturbance of exponential type.

We thus expect approximately permanent orbits, those near the axis being given by

$$\frac{r}{a} = \frac{1.4303}{n}$$
, where n is an integer not less than 2,

$$\frac{r}{a} = \frac{2.4590}{n}, \qquad 3,$$

and so on.

On the other hand, if they are near the equatorial plane, r/a takes the values

$$\frac{r}{a} = \frac{0.87334}{n}$$
, where n may now begin at 1,

$$\frac{r}{a} = \frac{1.97470}{n}$$
, , , 2,

and so on.

Corresponding to these we have, if the orbits are close to the axis, series of the usual Balmer type. The first series is given by frequency,

$$\nu = -\frac{1}{2\pi} \omega = -\frac{1}{2\pi} \cdot \frac{e\mu_2}{ma^3} + \frac{5}{2\pi} \cdot \frac{e\mu_1}{ma^3} \left\{ 1 - \frac{3}{5} \cdot \frac{(1.4303)^2}{n^2} \right\}.$$

For those near the equatorial plane we should have to use the expressions involving square roots, and limits are set to the number of lines.

We may expect these series of magnetic type to be more diffuse than those of electric type. It is, of course, obvious that disturbances of higher order may arise, and that the series only have approximate permanence, since those selected as permanent for disturbance of electric type are not permanent for disturbance of magnetic type and vice versa. This, however, suggests a basis of explanation for the presence or absence of certain series according to the source of excitation. And it may be noticed that while the two types of series cannot exist together, they might both be exhibited photographically if the exciting disturbance changes at optically long intervals from one type to the other.

We may now compare with observed results the simpler formulæ which hold when the orbits lie near the axis. They appear to have a direct application to certain cases, although we ought not to lose sight of the more complex expressions arising from equatorial orbits, which probably have a wider application.

We have, then, the various series of Balmer type, of which the first is given by

$$\nu = -\frac{1}{2\pi} \cdot \frac{e\mu_2}{ma^3} + \frac{5}{2\pi} \cdot \frac{e\mu_1}{ma^3} \left\{ 1 - \frac{3}{5} \cdot \frac{(1\cdot4303)^2}{n^2} \right\} \quad (n = 2, 3, 4, \text{ etc.}).$$

and the series of more general Rydberg type,

$$\nu = -\frac{1}{2\pi} \cdot \frac{e\mu_1}{ma^3} + \frac{5}{2\pi} \cdot \frac{e\mu_2}{ma^3} \left\{ 1 - \frac{3}{5} \cdot \frac{(1\cdot4303)^3}{p^2} \right\} ,$$

in which p takes the values 1.4303, 2.4590, etc., while the higher values approximate to the well-known form $n+\frac{1}{2}$, where n is an integer. It may prove crucial that the lower values differ considerably from $n+\frac{1}{2}$.

For general exploratory purposes it may be useful to note that the numbers,

$$(1.4303)^2$$
, $(2.4590)^2$, etc.,

are very nearly the whole numbers

$$2, 6, 12, 20, 30, 42, \ldots, n(n+1)$$

although for exact comparison these would not be sufficiently accurate.

If we write $\mu_1 = (1-k)\mu$, $\mu_2 = k\mu$, where k < 1, we find that the tail of

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both the Balmer and Rydberg series is the same, viz., $\nu_{\infty} = \frac{5}{2\pi} \cdot \frac{e\mu_1}{ma^3} \cdot \frac{(5-6k)}{5(1-k)}$ and since we cannot admit a negative value k must be $<\frac{5}{6}$. When the value of k is determined, we must take the heads of the series (in general different) as the last one which keeps ν positive. For a positive value of ω means that the corresponding orbit of the same angular momentum is impossible. Its place is taken by a corresponding extension of the region of possible equatorial orbits. It would seem fairest to suppose that our model corresponds to the elementary hydrogen atom.

In his recent Bakerian lecture, and in a private letter to me, Prof. Fowler now entertains the view that the hydrogen spectrum contains only series expressed by Balmer's formula, and that the extensive series of lines formerly* attributed to hydrogen are better represented by an extended Balmer formula, and do not represent hydrogen. I adopt his view, as I feel that this matter of arranging lines in series is one which can only be undertaken with advantage by those having intimate personal experimental knowledge of the spectra.

Rydberg's constant in wave numbers is 109675, which we may call N. The question now arises, which of the series of Balmer type in our formula is the one which gives N? That is to say, shall we take $\frac{5}{2\pi}$. $\frac{e\mu_1}{ma^3}$ as

 $\frac{5}{3(1\cdot4303)^2}$ N. 3×10^{10} , $\frac{5}{3(2\cdot4590)^2}$ N. 3×10^{10} , or etc.? It makes no difference to the sequence of differences obtained or to the tail of the series, and the only effect on the principal series is to strike out in succession the lines at the head.

Thus, if we take $\frac{5}{2\pi}$. $\frac{e\mu_1}{ma^3} = \frac{5\,\mathrm{N}}{3\,(1\cdot4303)^3} \times 3 \times 10^{10} = 89352 \times 3 \times 10^{10}$, and try to represent the experimental wave numbers 15237,20570,23038,..., 27423, we get $\frac{5-6\,k}{5\,(1-k)} \times 89352 = 27423$, or $k=\frac{7}{9}$ nearly, and the principal Balmer series is

$$n=2$$
. $n=3$. $n=4$. $n=5$. $n=\infty$. 4 , 15239, 20568, 23036, ..., 27423.

If we take

$$\frac{5}{2\pi} \cdot \frac{e\mu_1}{ma^3} = \frac{5N}{3(2.4590)^2} \times 3 \times 10^{10} = 30230 \times 3 \times 10^{10},$$

we have

$$\frac{5-6k}{5(1-k)} \times 30230 = 27423$$
, or $k = \frac{1}{3}$, nearly,

^{* &#}x27;Monthly Notices, R.A.S.,' vol. 73, pp. 67 and 68.

and the principal Balmer series is exactly as before with the first member 4 struck out. I cannot guarantee the accuracy of the fifth figure.

If our view is correct, we ought to expect that, under certain circumstances, there should be a series approximating to the Rydberg type. Whichever of the two cases above we select we get the following values:—

9285, 18319, 21952, 23773, 24815, ..., 27423.

Subsidiary series of both types are to be expected and may be computed. These differ according to the assumption as to the principal series, so that discrimination may be possible; but it is clearly more important to settle the question of the first series of Rydberg type.

If now we take $e/m = 1.7 \times 10^7$, $\mu = 1.8 \times 10^{-21}$, the first supposition as to the Rydberg constant gives $a = 1.2 \times 10^{-10}$, and the second $a = 2.6 \times 10^{-10}$, the distribution of μ differing in the two cases. The angular momentum of the particle cannot exceed 4×10^{-5} of Planck's unit 6.8×10^{-27} .

We may summarise the results by saying that within a nucleus possessing the usual positive electronic charge and possessing fixed magnetic moment of the value attributed to the magneton, we may have approximately permanent orbits of corpuscles with the usual value of e/m which give rise to series of spectral lines of recognised type. They are probably diffuse and have no Equatorial orbits also give rise to series of the same general structure. character. These are not expressible in so concise a form; the number of lines is limited and may be expected to possess a fourfold structure. Here we may consider the question of the Zeeman effect. equation for the equatorial orbits shows at once that the Zeeman effect of the usual type may be expected to arise. But the orbits of the same angular momentum, although affected by an external magnetic field, do not give structural Zeeman effect, but only an additional general diffuseness.

The radius of this nucleus required to give suitable optical values is of order 10⁻¹⁰, which is considerably smaller than the usual estimate of the atomic radius.

The wave-length of the rapidly damped disturbance communicated by this nucleus to the exterior is $4\pi a/\sqrt{3}$, which is rather smaller than the value assigned to characteristic Röntgen radiation. It is, however, not a little curious that the wave-length of the radiation from a corpuscle just outside the nucleus comes out about 2×10^{-8} , and this is sufficiently near observed values.

The effective radius of an atom for external purposes is, as we have said, usually estimated at about 10⁻⁸.

Our results would not be affected if there is an outer shell extending to this distance, provided the inner nucleus is admitted. But one would prefer to have only one radius in specifying the atom. The value 10^{-8} depends largely on the kinetic theory of gases for hard spheres, and is admittedly rather weak. It is conceivable that some explanation is possible depending on the range of possible external corpuscular orbits at a given temperature. Meanwhile it is a point requiring consideration.

It may be added that, when the nucleus is free to move, corrections will be introduced in the formulæ we have obtained which depend on the mass of the nucleus.

Sir Joseph Larmor has very kindly discussed these results with me, and has suggested several important improvements of statement that have been adopted.

Electromagnetic Waves in a Perfectly Conducting Tube.

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The problem of waves in conducting tubes has already been treated by various authors.* Nevertheless, the solutions here proposed, offering certain peculiarities with respect to the velocity of the corresponding waves, and partly also with respect to the shape, and distribution of the lines of force, seemed worthy of notice.

Let z be measured along the axis of an infinite right cylindrical tube of circular section. The material of the tube is assumed to be a perfect conductor, its interior being empty or filled with air. The electromagnetic waves will be assumed throughout to be axially symmetrical and of permanent type, i.e. to conserve all their features while proceeding along the tube.

If r be the distance of a point from the z axis, further, R and Z the

* J. J. Thomson, 'Recent Researches in Electricity and Magnetism,' 1893; Lord Rayleigh, 'Phil. Mag.,' vol. 43, p. 125 (1897); R. H. Weber, 'Ann. der Physik,' vol. 8, p. 721 (1902). Art account of the experimental investigations by v. Lang, Drude and Becker will be found in a paper by A. Kalähne, 'Ann. der Physik,' vol. 18, p. 92 (1905). Kalähne's own theoretical investigations concern only a ring-shaped tube.

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transversal and the longitudinal components of the electric force, M the magnetic force, and r the velocity of light in vacuo, then Maxwell's equations are:—

$$\frac{\partial (rZ)}{\partial t} = c \frac{\partial}{\partial r} (rM); \qquad \frac{\partial (rR)}{\partial t} = -c \frac{\partial}{\partial z} (rM),$$

$$\frac{\partial}{\partial z} (rZ) + \frac{\partial}{\partial r} (rR) = 0,$$

$$\frac{\partial M}{\partial t} = c \left(\frac{\partial Z}{\partial r} - \frac{\partial R}{\partial z} \right).$$

The lines of magnetic force are circles normal to and centred on the axis of symmetry, M being reckoned positive when the magnetic line is in the right-handed screw relation to the axis of positive z. By axial symmetry, M is constant along each magnetic line, so that the corresponding solenoidal condition is already fulfilled. The lines of electric force are wholly contained in the meridian planes.

The first three of the above equations are satisfied, in the well-known way, by

$$rZ = \frac{\partial \psi}{\partial r}, \quad rR = -\frac{\partial \psi}{\partial z}, \quad rM = \frac{1}{c} \cdot \frac{\partial \psi}{\partial t},$$
 (1)

and the fourth equation gives for ψ , known as Stokes' current function, the differential equation

$$\frac{1}{c^2} \cdot \frac{\partial^2 \psi}{\partial t^2} = \frac{\partial^2 \psi}{\partial z^2} + r \frac{\partial}{\partial r} \left(\frac{1}{r} \cdot \frac{\partial \psi}{\partial r} \right).$$

The equation to any line of electric force is $\psi = \text{const.}$ It is convenient to introduce an auxiliary function ϕ , such that

$$\psi = r \frac{\partial \phi}{\partial x}.$$
 (2)

Then the equation for ϕ is

$$\frac{1}{c^2} \cdot \frac{\partial^2 \phi}{\partial t^2} = \frac{\partial^2 \phi}{\partial z^2} + \frac{1}{r} \cdot \frac{\partial}{\partial r} \left(r \frac{\partial \phi}{\partial r} \right). \tag{3}$$

The only condition yet to be satisfied at the surface of the tube is Z=0, i.e. $\partial \psi/\partial r=0$, or

$$\frac{\partial}{\partial r} \left(r \frac{\partial \phi}{\partial r} \right) = 0, \text{ for } r = \alpha, \tag{4}$$

a being the radius of the tube's section.

Thus, the most general axially symmetrical electromagnetic field in a perfectly conducting tube is given by the function ϕ satisfying (3) and (4).

Let us now require that the waves should be of a permanent type, i.e. that the whole network of electric and magnetic lines should move along the tube, with a constant velocity v, without being deformed. This amounts to writing

$$\phi = \phi(r, \zeta),$$

where $\zeta = z - vt$, the value of v being thus far left undetermined. Under such conditions it is enough to consider the state of things at one single instant, say, t = 0. Thus equation (3) will become

$$\left(1 - \frac{v^{s}}{c^{2}}\right) \frac{\partial^{2} \phi}{\partial z^{s}} + \frac{1}{r} \cdot \frac{\partial}{\partial r} \left(r \frac{\partial \phi}{\partial r}\right) = 0, \tag{3a}$$

and the surface condition (4) will assume the form

$$\left(1-\frac{v^2}{c^2}\right)\frac{\partial^2\phi}{\partial z^2}=0,$$

for r=a.

But the case of critical velocity, v=c, must obviously be discarded. In fact, it would lead at once to $\psi=r\partial\phi/\partial r=g(z)$, where g is a function of z alone, and consequently to Z=0 and R=-g'(z)/r, which is incompatible with the conditions of the problem, unless g'=0, when there is no field. Thus, the only possible waves of the specified kind are characterised by

$$v \neq c$$
.

The surface condition becomes, therefore,

$$\left(\frac{\partial^2 \phi}{\partial z^2}\right)_{z=a} = 0. \tag{4a}$$

Equations (3a) and (4a), with $v \neq c$, contain the most general axially symmetrical waves of permanent type.

Out of these let us consider such only as are simply periodic in time, and therefore also with respect to z, that is to say, let us take ϕ of the form

$$\phi = \sin(mz)\,\omega(r),\tag{5}$$

where m is any real constant, and ω a function of r alone. Write

$$\kappa = m\sqrt{(v^2/c^2 - 1)},\tag{6}$$

$$x = \kappa r. \tag{7}$$

Then (3a) gives for ω Bessel's differential equation, of the zero order,

$$\frac{d^2\omega}{dx^2} + \frac{1}{x} \cdot \frac{d\omega}{dx} + \omega = 0, \tag{3b}$$

and the boundary condition (4a) assumes the form

$$\omega(\kappa a)=0.$$

The well-known general integral of (3b) is

$$\omega = AJ(x) + BK(x),$$

where J, written shortly for J_0 , is Bessel's function of the first kind, of the zero order, and K, Bessel's function of the second kind,* while A and B are arbitrary constants. On the axis of the tube J remains finite, i.e. J(0) = 1, but K becomes infinite for x = 0. We are thus reduced at once to

$$\phi = A \sin(mz) J(\kappa r), \tag{8}$$

with the condition

$$J(\kappa a) = 0. (9)$$

The latter equation determines the admissible values of κ .

Now, all the roots of the transcendental equation J(x) = 0 are real; therefore, by (6), and since m has been supposed real, the velocities of transfer along the tube of the corresponding waves will all be greater than the velocity of light, *i.e.*

$$v > \epsilon$$

for each of the roots. This constitutes a peculiar feature of all the waves of the specified kind.

Let us denote the roots of the equation J(x) = 0, arranged in the order of ascending value, by x_1, x_2 , etc., in general by x_i ; thus, to five decimal figures,

$$x_1 = 2.40483$$
, $x_2 = 5.52008$, $x_3 = 8.65373$, etc.

Then the corresponding values of κ will be

$$\kappa_i = \frac{x_i}{a},\tag{10}$$

whence, for any prescribed m, the corresponding value $v = v_i$ will follow.

It will be remembered that (8) refers to a single instant, t = 0. For any t, the variable z has simply to be replaced by $\zeta = z - vt$. If T be the period of vibration, and $\lambda = vT$, the corresponding wave-length,

$$T = \frac{2\pi}{mv}, \qquad \lambda = \frac{2\pi}{m}.$$

It will be convenient, henceforward, to consider the time-period of vibrations as given; or what amounts to the same thing mv, and not m itself. On the other hand we are given κ , by (10). Eliminating m_i from the equations

$$m_i v_i = \frac{2\pi}{T}, \qquad m_i^2 \left(\frac{v_i^2}{c^2} - 1\right) = \frac{x_i^2}{a^2},$$

we obtain the set of velocities in terms of T alone,

$$v_i = c / \sqrt{\left[1 - \left(\frac{x_i}{2\pi} \cdot \frac{c\Gamma}{a}\right)^2\right]}, \quad i = 1, 2, ...,$$
 (11)

* A known expansion of this function, for complex values of x, is

$$\mathbb{K}(x) = \mathbb{J}(x) \left[\log \frac{2}{x} + \frac{i\pi}{2} + \mathbb{C} \right] - 2J_2(x) + J_4(x) - \frac{2}{3}J_6(x) + \dots,$$

where C = 0.577....

whence also $m_i = 2\pi/\mathrm{T}v_i$, and

$$\phi_i = A \sin \left(m_i \zeta_i \right) J \left(x_i \frac{r}{a} \right), \quad \zeta_i = z - v_i t; \quad (12)$$

and therefore also, by means of (1) and (2), the corresponding electromagnetic field in the tube.

There is thus, generally speaking, for every given period T, a whole series of differently shaped waves which will proceed along the tube with different velocities, v_1, v_2, \ldots , without distortion. These, corresponding to the roots x_1, x_2, \ldots , and to the given period T, may be called waves of the first, the second, etc., order, respectively.

Let λ_0 be the normal wave-length, *i.e.* the wave-length which would correspond to the given period in free space, and let ϵ be the ratio of this length, $\lambda_0 = cT$, to the circumference of the transversal section of the tube,

$$\epsilon = \lambda_0 / 2 \pi a. \tag{13}$$

Then the velocity of the corresponding wave of the ith order will be

$$v_i = c/\sqrt{(1 - \epsilon^2 x_i^2)}. \tag{14}$$

The lower limit of v_i , which is approached when ϵ shrinks indefinitely, is the velocity of light, ϵ , while there is no upper limit to v_i , whose value grows indefinitely when ϵ tends to $1/x_i$. Notice that for $\epsilon > 1/x_i$ we should have an imaginary v_i , so that $\sin (m_i \xi_i)$, and $\cos (m_i \xi_i)$, would degenerate into products of trigonometric and of exponential functions, and taking either their real or their imaginary parts, the resulting ϕ_i would increase indefinitely along the positive or the negative axis of z. Such solutions, therefore, must be physically rejected.

If the order (i) of the waves be given, we are confined to such vibrations for which the value of ϵ does not exceed $1/x_i$. Conversely, for any given value of the ratio $\epsilon = \lambda_0/2\pi a$ waves of the specified kind are possible only up to the highest order, for which

$$x_i < 1/\epsilon. \tag{15}$$

Thus, for $\epsilon=0.1$ (i.e. for $\lambda_0=0.628a$) we have only waves of the first, second, and third order, since the fourth root of J(x)=0 is greater than 10, to wit, $x_4=11.7915$. For $\epsilon=1/30$ we would have nine different waves (since $x_0=27.4935$, $x_{10}=30.6346$), and for $\epsilon=0.01$ as many as thirty-two waves of different orders ($x_{32}=99.7468$, $x_{33}=102.8884$). For $\epsilon>1/x_1$, i.e. roughly for

 $\epsilon > 0.42$

there are no waves possible of the kind here considered.

Keeping this in mind, let us consider the field corresponding to any

particular solution ϕ_i of the form of (12). Omitting, for the sake of brevity, the suffix i everywhere, with the exception of x itself, we have, by (2), and remembering that $J'(x) = -J_1(x)$,

$$\psi = -A \frac{x_i r}{a} J_1 \left(\frac{x_i r}{a} \right) \sin \left(m \zeta \right), \tag{16}$$

so that the equation to any line of electric force, say, for t = 0, will be

$$\sin(mz) r J_1\left(\frac{x_i r}{a}\right) = C, \qquad (17)$$

where C is a constant. The state of things at any instant t will be obtained by simply shifting the whole network of lines of force a distance vt along the axis of the tube.

The electric and magnetic forces will be, by (1), and by (3a),

$$Z = \frac{\kappa^2}{m^2} \cdot \frac{\partial^2 \phi}{\partial \zeta^2} = -A \left(\frac{x_i}{a} \right)^2 \sin \left(m \zeta \right) J \left(\frac{x_i r}{a} \right),$$

$$R = A \frac{m x_i}{a} \cos \left(m \zeta \right) J_1 \left(\frac{x_i r}{a} \right),$$

$$M = \frac{v}{c} R = R \left(1 - \epsilon^2 x_i^2 \right)^{-\frac{1}{2}},$$
(18)

where $\epsilon = cT/2\pi a$, as above. For r=a, the longitudinal electric component Z is nil, as it should be. The radial electric component R, although proportional to, is generally different from the absolute value M of the magnetic force; they become approximately equal to one another only for relatively short vibrations and for not excessively high orders (i) of waves. The densities of the electric and of the magnetic energy are, generally speaking, not equal to one another. In short, the waves under consideration are not pure waves. At the axis of the tube, i.c. for r=0, J=1, while J_1 vanishes, so that, for any axial point,

$$Z = -A \left(\frac{x_i}{a}\right)^2 \sin{(m\zeta)}, \qquad R = M = 0.$$
 (18a)

Thus the axis of the tube is itself a line of electric force, or, more exactly, a chain of such lines of intermittently positive and negative sense, each of these straight lines of force stretching over the length $\frac{1}{2}\lambda$, e.g. between pairs of consecutive points defined by

$$m\zeta = n\pi$$
, $(n+1)\pi$,

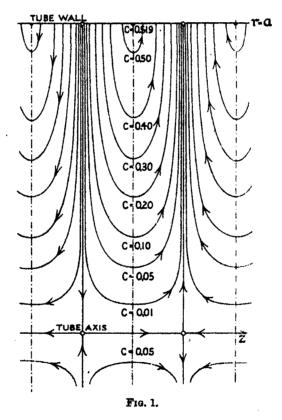
where n is any integer. All of these are neutral points, i.e. points of vanishing electric force (R = Z = 0). They share, of course, in the motion of the whole field with the velocity $v = v_i$.

From (18) we see also that the axial electric component Z vanishes for

 $\sin(m\zeta) = 0$, for all values of r, while the radial component assumes the value $\pm Amx_iJ_1/a$. Thus, all the radii of each cross-section of the tube passing through a neutral point are again lines of electric force, viz., corresponding to $\psi = C = 0$. These are the only transversal lines of electric force.

By the aid of formula (17) a set of z values corresponding to different values of r/a, from 0 to 1, for different C's and prescribed values of ϵx_i , can easily be calculated and plotted against one another. In this way the following pair of figures has been drawn.* In both of them the scale used for z is the same as that for r, and both refer to $\epsilon = \lambda_0/2\pi a = 0.1$.

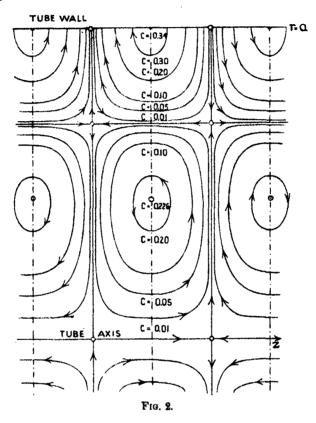
Fig. 1 shows the lines of electric force for waves of the first order, i.e.



for $x_i = x_1 = 2.405$; the diagram stretches over a whole wave-length, $\lambda_1 = v_1 T = 0.647a$. The neutral electric points are marked by small circles. Fig. 2 gives the lines of force for waves of the second order, i.e. for

^{*} Figs. 1 and 2 are reproduced from the author's treatise on 'Electricity and Magnetism' (Polish), vol. 2. Warsaw, 1910.

 $x_2 = 5.520$. The corresponding wave-length is $\lambda_2 = v_2 T = 0.753a$. In this case we have neutral points not only on the axis and at the surface of the tube, but also on the straight line r = 0.694a, parallel to the axis, the segments of this line being again lines of electric force. Moreover, there is a neutral point between this line and the axis, in each of the complete



rectangles. Each of these points, being rotated round the axis, gives rise to a circular neutral line, of course.

In the case of fig. 1, the argument x_1r/a moves within the limits 0 and 2.405; in this interval the function J_1 does not change its sign, and the system of electric lines of force is correspondingly simple; none of them is closed, each begins and ends at the surface of the tube. In the case of the waves of second order (fig. 2) the argument of J_1 , i.e. x_2r/a , moves within considerably wider limits, from 0 to 5.520, between which J_1 undergoes a single change of sign, thus giving rise to the supplementary neutral points at the distance 7a/10 from the axis (in round figures), and originating two

^{*} This being a root of $J_1(rx_2/a) = 0$.

rectangles of breadth $\lambda_2/2$, one, based upon the axis, of height 7a/10, and another of height 3a/10, extending to the surface of the tube. In the former rectangle all lines of force are closed, while in the latter rectangle all of them begin and end at the surface of the tube, as in the case of fig. 1. For waves of the third and higher orders we would obtain more such rectangles, in correspondence to the number of changes of sign experienced by J_1 in the intervals from 0 to x_3r/a , and so on. But this would not introduce any essentially new features into the system of lines of force. The above two figures will therefore be sufficient.

Returning to (18), we have, for the axial and the radial components of the flux of energy, $F_x = cRM$, $F_r = -cMZ$,

$$F_{z} = vR^{2} = A^{2}v \left[\frac{mx_{i}}{a} \cos(m\zeta) J_{1} \right]^{2},$$

$$F_{r} = -vRZ = \frac{1}{2}A^{2}mv \left(\frac{x_{i}}{a} \right)^{3} \sin(2m\zeta) JJ_{1},$$
heth the Bernel functions being a π/π . Instead of we we

the argument of both the Bessel functions being $x_i r/a$. Instead of mv we may write here $2\pi/T$. Since $J_1 = 0$ for r = 0, the flux of energy vanishes at all axial points. At the surface of the tube $F_r = 0$, as it should be. Remembering that the lines of energy flux are everywhere orthogonal to those of electric force (and contained in the meridian planes), the reader can easily draw them for himself. It may be interesting to notice that, whereas the radial flux is now towards and now away from the axis, the axial flux of energy, F_z , is always positive (for v>0), i.e. always in the direction of transfer of the waves.

Substituting in the general formula (14) the value 1/10 for ϵ and the quoted numerical values of x_1 , x_2 , we obtain, to three decimal figures,

$$v_1 = 1.030 c, \qquad v_2 = 1.199 c,$$

for the velocities of the waves represented in figs. 1 and 2 respectively. For $\epsilon = 1/10$ there exists but one more wave of the specified kind, viz., that of the third order, corresponding to $x_3 = 8.654$; its velocity is nearly twice that of light, more accurately

$$v_2 = 1.996c$$

For sufficiently smaller values of ϵ we would obtain more waves of different orders, to which greater velocities would correspond. All these waves, corresponding to a fixed value of $\epsilon = c T/2\pi a$, can be superposed; but, their velocities being different, the resultant wave will, of course, split at once into its components. On the other hand, a compound wave of permanent type can be obtained by the superposition of an indefinite number of simple waves

of both different periods T and different orders, subject to the condition $\epsilon x_i = \text{const.}$, the components thus defined constituting a discrete set.

Finally, we may have a superposition of a continuous manifold of simple waves, (12), of a fixed order, say n, but of different periods T, ranging over a continuous interval $0 < T < 2\pi a/x_n$. Then the resultant train of waves, while moving past the tube, will undergo continuous deformations. The train of waves as such has no unique velocity, but we can in this case speak of the group-velocity,

$$V = v - \lambda \frac{dv}{d\lambda}, \tag{20}$$

in the neighbourhood of any given value of wave-length $\lambda = vT$. By (14), v can be written, in terms of λ ,

$$v = c\sqrt{(1+\alpha_n^2\lambda^2)}, \qquad (21)$$

where $a_n = x_n/2\pi a$ is a fixed magnitude, whence, by (20),

$$V = c/\sqrt{(1 + \alpha_n^2 \lambda^2)}. \tag{22}$$

Thus, although for each individual component v > c, the group-velocity, in the vicinity of any value of λ , is smaller than the velocity of light in free space.

A superposition of this kind can be used to represent a wave of discontinuity or a thin electromagnetic pulse or "Röntgen wave," provided that these are axially symmetrical. Such a wave, supposing that it is neither being split into two or more nor dispersed, can propagate itself only with the velocity c; this property belongs to each surface-element of the wave, taken separately, and is therefore independent of any boundary conditions.* In our present case, a surface of discontinuity, if produced in the tube at a given instant, would disperse at once, since its component simple waves have different velocities. A thin electromagnetic pulse, while moving past the tube, would be broadened or drawn out. Accordingly we should expect that "hard" Röntgen rays (of axially symmetrical structure), sent through a conducting tube, will be "softened." I do not know whether experiments to that purpose are worth undertaking.

* Cf. 'Ann. der Physik,' vol. 26, p. 751 (1908); vol. 29, p. 523 (1909).

The Analysis of Gases after Passage of Electric Discharge.

By A. C. G. Egerton.

(Communicated by Prof. J. N. Collie, F.R.S. Received June 10, 1914.)

Introduction.

It has been found by Collie and Patterson* that, after the passage of the electric discharge through pure hydrogen in a vacuum tube at low pressure, small quantities of helium and neon could be detected in the gas pumped out of the discharge tube. These gases were shown not to be present in the hydrogen which was let into the discharge tube. They must, then, either originate from—(i) occlusion of air in the glass or electrodes, or (ii) from the outer air during the experiment or the subsequent analysis, or (iii) be actually formed by some transmutation process due to the action of the discharge. In the latter case the seat of the effect of the discharge may be at the solid electrode, glass walls, or in the gas itself. The experiments of the above authors appear to show that:—

- (i) The gas did not originate from occlusion in the electrodes or glass walls, because these gave no such rare gases on solution and subsequent analysis of the gases.
- (ii) The gases did not enter from the outer air, because similar effects were obtained when the tube was jacketed by another tube, the space between the two being evacuated. Sometimes, also, only helium was obtained, whereas neon would be expected if air had leaked in.
- (iii) The gas was not formed by some change at the electrodes, as similar effects were obtained (though to a lesser extent) by means of an electrodeless discharge.

The result of the work indicated, then, that the hydrogen (or possibly the glass tube) had in some way been affected by the discharge, so as to obtain helium or neon. It is noteworthy that positive results of the production of He or Ne are only sometimes obtained. J. J. Thomson† had noticed that helium lines were always very marked in the positive ray spectrum produced during the bombardment of metallic substances by cathode rays, when only pure hydrogen had been allowed to enter the discharge tube. He favoured the view that the metallic electrodes were responsible for the production of the helium, and that it might have been formed by slow radioactive processes and only liberated by the cathodic bombardment. Subsequently the Hon. R.

^{* &#}x27;Chem. Soc. Trans.,' vol. 103, p. 419; and 'Chem. Soc. Proc.,' vol. 29, p. 217 (1913).

^{+ &#}x27;Nature,' vol. 90, p. 645 (1913).

Strutt made a short investigation of the subject,* but obtained no trace of helium or neon in the gas, which was analysed after passage of the discharge. He further showed that a minute quantity of air could be detected by means of the residual neon (after getting rid of hydrogen by sparking with oxygen, and absorbing the residual gas by means of cooled charcoal). He held that the gases could not be safely transferred by means of small inverted tubes over mercury, without the possibility of a trace of air entering during the process: and this led him to construct an apparatus which was entirely self-contained, and by means of which all external transference from the discharge tube to the analysis apparatus was entirely avoided.

The work of these investigators has not, therefore, led to similar results, and the following questions present themselves:—Firstly, were the electrical conditions of Strutt's experiments unfavourable to the formation of rare gases? Secondly, was the method of analysis less sensitive? Thirdly, is it possible to prevent access of air into the apparatus during the experiment and analysis, and to entirely free the electrodes of all detectable traces of rare gases?

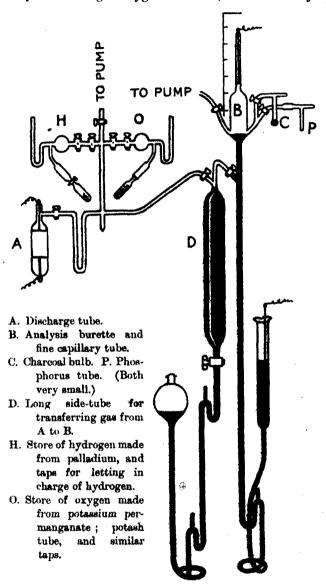
In the work to be described, which was carried out in continuation of some other work along similar lines, special attention has been paid to these points: the electrical conditions were varied considerably by altering the generating apparatus and the shape of the discharge tubes; the method of analysis was made as sensitive as possible and blank tests were frequently applied. The result, unfortunately, has not thrown any light on the production of the rare gases, as these gases were not obtained when the tube and electrodes had been evacuated as far as possible, and when there was no detectable leakage of air in the apparatus.

Experimental.

In continuation of some former work the apparatus depicted was built. It has been found that when the gases were pumped out of the discharge tube and transferred by means of small tubes to the analysing burettes, as often as not, traces of argon could be detected. This argon was traced to some mercury; by means of tube D, this difficulty was overcome and the gases could be brought directly and completely into the analysing burette from the discharge tube without coming into contact with mercury, which stands in the presence of air. The presence of about of 0.1 cu. mm. of air can be detected by the argon. The nitrogen is often not found unless larger quantities of air are present, as ozone is formed during the analysis and combines with the nitrogen and mercury; phosphorus, too, absorbs

small quantities of nitrogen. Neon was only found when much larger quantities of air were present.

For the analysis of the gas oxygen is added, the burette is jacketed with



a small cup of liquid air, and the discharge is passed; water and ozone are formed and a high vacuum is obtained (ozone partly condensing and partly combining with the mercury). The tube and the mercury are then warmed and oxygen absorbed by opening to the phosphorus or charcoal. Sometimes

a small quantity of oxygen and carbon oxides remain unabsorbed, these disappear on passing the discharge through the capillary jacketed by liquid air, owing to the formation of ozone; any small residual quantities of nitrogen or of hydrogen also disappear owing to this. In order to be sure that none of the rare gases are hidden, the mercury is warmed, the process of analysis repeated, and the spectrum of the residual gases carefully examined. In the final experiment the hydrogen and oxygen were sparked at ordinary pressure by means of two platinum wires sealed in the burette.

The following experiments are some of those that have been made with this apparatus:—

- (a) The discharge tube was a cylindrical tube with two disc electrodes placed opposite each other. A 6-inch coil with hammer break was used. Gas analysed by phosphorus—No Ne or He found.
- (b) Another similar tube. A 9-inch coil with a long spring hammer break. Gas analysed by phosphorus—No A, no He, no Ne found.
- (c) A similar tube but with both anti-cathode and anode. A large 20-inch coil, Caldwell electrolytic break, plate and point rectifier in the circuit. Gas analysed similarly—Trace A, no Ne, no He. (This merest trace of argon came from the oxygen used for the analysis.)
- (d) A tube with large spiral aluminium wire as cathode, anode in a small side bulb connected with the narrow tube, the tube acting in some measure as a rectifier. A 20-inch coil, electrolytic break and rectifier, also a 9-inch coil and two types of hammer break. Analysed by charcoal—No Ne or He (experiment lasted 22 hours).
- (e) A tube with two platinum electrodes ½ cm. by 2 mm. in two glass bulbs (4 cm.) connected by a narrow tube. Gas analysed by charcoal:—
 - 1. A 9-inch coil, hammer breaks and rectifier-No Ne or He.
 - 2. A 20-inch coil, hammer break in series-No Ne or He.
 - 3. A 20-inch coil, electrolytic break and rectifier—No Ne or He.

In this experiment there was much "splashing" from the cathode; in the last part of the experiment the cathode was often bright red hot.

- . (f) Similar tube, aluminium anodes, platinum cathodes. A 20-inch coil, electrolytic break and rectifier. Very much "splashing." Gas analysed by charcoal—No Ne or He.
- (g) Spectrum-shaped tube; palladium rod anode, palladium plate cathodes, a 9-inch coil and a hammer break. There was so much "splashing" that a larger coil could not be used. Gas analysed by charcoal—No Ne or He.
- (h) One cubic centimetre was pumped out of a large Röntgen tube, through which the heaviest obtainable unidirectional discharge had been passed for

four hours (5 milliampères, between 60,000 and 120,000 volts)—No Ne or He was detected.

In another experiment a little argon was detected, but no Ne or He. A third quantity, which was known to be contaminated by air, was analysed by charcoal and gave a considerable quantity of neon. (I have to thank Dr. Lindemann for these samples of gas.)

- (i) A spectrum tube with fine platinum wire cathode, a 9-inch coil, hammer break and rectifier. Analysed by phosphorus—No Ne or He, a trace of argon (due to oxygen).
 - (j) A spectrum tube with small bead of platinum as cathode.
- 1. A 9-inch coil and rectifier (six hours). Analysed by sparking in burette and phosphorus—No Ne or He.
- 2. A 20-inch coil, electrolytic break and rectifier (five hours, cathode becoming white hot at times). Both together analysed by phosphorus and afterwards by charcoal—A trace of He possibly, but such a small quantity that its presence was doubtful.

In all these experiments the tube was as strongly heated as possible when pumping out the gases, also during the preliminary exhaustion. The discharge was reversed occasionally, as it has been found that a cool anode will often absorb gas given off by a hot cathode. The tube was finally washed out with pure hydrogen. The duration of each experiment was about eight hours, unless otherwise stated. At a certain stage of exhaustion the hydrogen is shot very easily into the walls of the tube, provided the latter does not become too hot or the vacuum too low. Charges of hydrogen are let in, when necessary, from the place between the two taps provided for that purpose. The amount of hydrogen absorbed by the walls appears to depend on the temperature, the shape of the tube, the pressure of the gas, and the potential of the cathode during exhaustion. A long time is required to entirely rid the walls and electrodes of gases; if a stronger cathode discharge is passed through the tube it is generally possible to obtain more gas (hydrogen and a little oxygen). However, with small tubes and many washes with pure hydrogen, it is certainly quite possible to get rid of all detectable traces of air. Once, when a minute leak was present, it was noticed that the spectrum of nitrogen was not given for some minutes, but only that of oxygen; the tube had palladium electrodes. It would seem that very small quantities of nitrogen had been made active, and were absorbed by the metal deposited on the walls of the tube.

Summary of Experiments.—In the above experiments electric discharge has been passed with three different sized coils, three different types of interrupters, through various sized and shaped tubes, with palladium, platinum,

and aluminium electrodes of various shapes and sizes, the analyses of the residual gases being carried out by phosphorus and charcoal in various ways, but no change of the gases, such as the production of helium or neon, has disclosed itself.

Theoretical.

It will be interesting to enquire into the mechanism which could, perhaps, give rise to such a production of helium by means of the electric discharge, and to calculate approximately the amount of energy that would be needed. In the first place, suppose one assumes an association process, and let the helium be formed from a certain quantity of hydrogen. It is a consequence of relativity theory that the variation of the mass of a system is connected with the variation of the internal energy by the following:—

$$\Delta E = c^2 \Delta m \left(\frac{1}{\sqrt{(1-\beta^2)}} - 1 \right)$$
,

where x^2 is the square of the velocity of light, and the last term merely depends on the movement of the system relative to the observer, and can be neglected in this case.*

$$\triangle E = 9 \times 10^{20} (4 \text{ H} - \text{He}) = 9 \times 10^{20} (4.032 - 3.99)$$

$$= 3.6 \times 10^{19} \text{ ergs per gramme-molecule of helium formed, } i.e.$$

$$6 \times 10^{-5} \text{ ergs per atom of helium.}$$

Every 1/100 cu. mm. of helium formed (a detectable quantity) would therefore need 1.6×10^{10} ergs. An induction coil certainly might supply this total energy in an hour, but there are two important considerations. First, the energy is only conveyed in the form of charged particles, and there can hardly be particles possessing energy of the order of 10⁻⁵ ergs within a discharge tube; the energy of the hydrogen ion in the dark space being of the order 10⁻¹⁰ ergs, and that of the cathode particles on the average 10⁻⁹ ergs, (a cathode particle would have to move in a field of over 30 million volts to possess energy 6×10^{-5} ergs). Many particles would therefore have to act simultaneously or their effects be additive; this would increase enormously the time required to produce a detectable quantity of helium. The second consideration is that four hydrogen atoms or possibly two hydrogen molecules must meet in order to form helium, and the energy must either be supplied at the moment of encounter, or they must be altered previously in such a way that they will associate on encounter and form helium. It is possible to calculate the probability of the occurrence of such a collision.

The probability P2a of two atoms or molecules colliding in a time dt is

$$\frac{\mathbf{T}}{t}dt$$
,

where T is the duration of the collision, t the time between two collisions. But, according to kinetic theory,

$$t = \frac{1}{\pi \sigma^2 N pc},$$

 σ = the diameter of an atom,

p = pressure,

N = number of atoms per unit volume at normal pressure and temperature,

c = mean velocity;

and

$$T = \frac{2f\sigma}{c/2},$$

where f is the fraction of the diameter to which distance the atoms interpenetrate; f will be a maximum when $f = \frac{1}{2}$.

$$\therefore P_{2a} = 4\pi N p f \sigma^3 dt.$$

Putting in values-

 $N = 2.75 \times 10^{19}$ molecules per cubic centimetre,

p=1 mm.,

 $f = \frac{1}{2}$

 $\sigma = 2 \times 10^{-8}$ cm.,

$$P_{2a} \le 1.81 \times 10^{-6} dt$$

The frequency of collision is $\pi\sigma^2 Npc$, i.e. 8.7×10^6 times per second. The number of atoms per cubic centimetre at 1 mm. pressure is 3.6×10^{16} atoms. \therefore total number of collisions in a tube of 100 c.c. is 1.58×10^{25} per second. The probability that during a collision lasting

$$\frac{2f\sigma}{c/2} = \frac{2 \times \frac{1}{2} \times 2 \times 10^{-8}}{1.91 \times 10^{8}/2} = 2.09 \times 10^{-13} \text{ secs. (at 17° C.)},$$

the colliding atoms will be struck by n other atoms is

$$2.09 \times 10^{-13} \times (1.81 \times 10^{-6})^{\text{N}}$$

or for a fourfold collision

$$n=2$$
;

$$P_{4a} = 6.8 \times 10^{-26} dt$$

and the number of collisions per second in a tube of 100 c.c. will become

$$(6.8 \times 10^{-16})(1.58 \times 10^{25}) = 10.7$$
 per sec.

That helium can be produced by a fourfold collision of hydrogen atoms

* J. H. Jeans, 'Dynamic Theory of Gases,' p. 205.

under certain special conditions is therefore quite out of the question, for there would have to be at least 7.7×10^8 such collisions per second in order to produce a detectable quantity of helium in 10 hours.

There remains the possibility that the helium might be produced from the collision of hydrogen molecules under certain conditions. It is difficult to see what those conditions in an electric discharge tube could be, other than the effect of an electron upon them. So it is necessary to calculate the chance of a collision of a cathode particle with the molecules of hydrogen.

The probability of an electron colliding with an atom or molecule would be $P_e = T/t' = T\nu$ where $\nu =$ number of times an electron collides with an atom per second.

$$\nu = \frac{a \times 3 \times 10^{10}}{10e} \cdot \frac{1}{\lambda} \cdot \frac{1}{n},$$

where a = current in ampères,

l = distance between electrodes,

 λ = free path of electrons,

n = number of atoms in discharge tube.

The maximum value of T is σ/c' , where

c' = velocity of electrons,

 $\sigma = \text{diameter of atom.}$

But $c' = \sqrt{(2 \operatorname{Ve} \lambda/ml)}$, where V = potential between electrodes in E.S. units.

$$\therefore \quad T\nu = \frac{\sigma}{\sqrt{(2 \operatorname{Ve}\lambda/ml)}} \cdot \frac{a \times 3 \times 10^{10}}{10e} \cdot \frac{l}{\lambda} \cdot \frac{1}{n}.$$

But $\lambda = \frac{4\sqrt{2}}{\pi N p \sigma^2}$ and n = N p v, where v is volume;

therefore

$$P_e = 3 \times 10^9 \cdot \frac{a}{e} \cdot \frac{l^{3/2}}{v} \cdot \frac{\pi^{3/2} N^{\frac{3}{2}} p^{\frac{3}{2}} \sigma^4}{\sqrt{(256\sqrt{2} \text{ Ve/m})}}$$

Putting $a = 10^{-3} = 1$ milliampère.

v = 100 c.c.

l = 10 cm.

p = 1 mm.

 $V = 10^4 \text{ volts}$

$$P_* = 4.2 \times 10^{-18} dt$$

The probability that an electron should strike a simple collision of two hydrogen molecules, which lasts 2×10^{-13} secs., is therefore 8.4×10^{-31} , or as 1.58×10^{26} collisions take place per second, 1.3×10^{-5} atoms of helium might be formed per second, which would mean a detectable quantity in about 6×10^{11} years. Thus even a collision of an electron with two hydrogen

molecules would be an inadequate explanation of the formation of the helium much more so the collision of four hydrogen atoms at a time, which would produce only one atom in about 10^{11} years. Likewise it could be shown that insufficient helium would be formed to detect in a reasonable period of time, even if the unlikely suggestion is assumed that the atoms or molecules are so altered by collision with the electrons, that when they subsequently collide with each other they might form helium atoms; for the probability of an electron colliding with an atom is small $(4.2 \times 10^{-18} \, dt)$, and even when such a collision does occur, the molecules which have encountered electrons must collide with each other.

The above calculations make it clear that the helium cannot arise from changes in the gases within the discharge tube, unless the conditions within a vacuum tube are very different from what they are taken to be and are such as to increase enormously the number of collisions of electrons, atoms, ions or molecules. This result is arrived at both from considerations of the energy needed to effect such a change and also from considerations of the possible mechanism producing such a change.

Next, let some disintegration process be assumed; could the helium be formed by the disintegration of the metallic electrodes or of the oxygen, silica, and other constituents of the glass or gases (oxygen, CO, etc.) in the discharge tube? The atomic weight of mercury is 200.6 and if the atoms were entirely split up into helium atoms, energy of the order of 10⁻³ ergs would be required per atom (this follows as before from Einstein's theory). For oxygen or carbon the quantity might be somewhat less than 10⁻⁵ ergs but for most elements it would be considerably more. The chances of finding in a discharge tube particles possessing sufficient energy to bring about such complete disintegration is exceedingly small; the α -particle possesses energy 1.3×10^{-5} ergs but even this does not seem to appreciably disintegrate the atoms it meets with.* However, there is no reason to suppose that the atoms must be completely disintegrated. It is quite conceivable that a partial disintegration and liberation of a helium atom from certain less stable atoms might arise under conditions of electric stress such as are obtained in a discharge tube. Such effects should be most likely to occur with the heaviest elements or possibly with rare earths or potassium.

From the above considerations it is more probable that the production of rare gases would arise from a process of disintegration than of association. Although it is not possible to make these calculations without certain

^{*} It is possible the a-particle does possess sufficient energy to disintegrate some of the atoms it encounters (see Ramsay and Camerou, 'Chem. Soc. Trans.,' vol. 91, p. 1605- (1907)).

assumptions which are not definitely established, it is unlikely that the orders of the above results would be greatly affected by future work: radioactivity affords evidence of the internal energy of an atom agreeing with that obtained by calculation; every gramme-atom of belium produced from radium releases about 10^{-19} ergs.

Conclusion.

The attempt to produce rare gases (Ne and He) in accordance with the experiments of Collie and Patterson, by the passage of an electric discharge, has not been successful. Both from theoretical and experimental standpoints, it is held that if such a production has an origin other than from atmospheric contamination, the source must be looked for in some action on the solids which compose the discharge tube (electrodes or glass) rather than from the gases.

I am greatly indebted to my friend, Mr. F. A. Lindemann, for suggesting the method of calculating the probability of collision of electrons and atoms and of some of the samples of gas analysed. I have also to thank Prof. Nernst for his interest in these experiments carried out in his laboratory in Berlin. The experiments were conducted in continuation of work carried out with Sir William Ramsay on other lines but with somewhat similar apparatus, and to him and Prof. Collie I am grateful for the generous permission to publish the work.

An Electrically Heated Full Radiator.

By H. B. Krene, D.Sc., Assistant Lecturer in Physics at the University of Birmingham.

(Communicated by Sir Oliver Lodge, F.R.S. Received December 10, 1914.)

In a previous paper by the author* the value of the "radiation constant" of the Stefan-Boltzmann law was obtained, using an apparatus which fulfilled the condition of a full receiver; all previous determinations being open to objection on the ground that this condition was not attained. The "emitter" used in that investigation and maintained at a temperature of 1100° C. was of the usual type—a modified form of Hereus furnace; but it was pointed out at the time that such a radiator is by no means a uniform temperature enclosure, and that the author intended to construct such an enclosure which would approximate more nearly to the ideal full radiator.

The value of the radiation constant is open to criticism until it has been determined with apparatus in which both "emitter" and "receiver" fulfil "black body" conditions.

The present paper describes an electrically heated high temperature full radiator, for which there is such a pressing need in full radiation measurements.

The Form of the Radiator.—The radiator consists of a bottle-shaped crucible of alumina with a cylindrical body 8 inches in diameter, and with conical ends and circular aperture B (fig. 1). The crucible was wound with platinum strip for electrical heating in a manner to be described later.

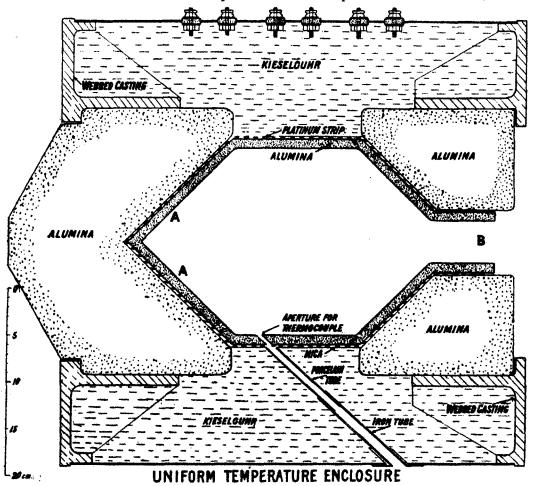
This form of radiator is preferable to the sphere, as it somewhat simplifies the difficulty of the electrical winding, although considerable difficulty was experienced in winding the conical ends. A further advantage consists in the fact that the region A, which will be "visible" from the receiver, loses less radiation to the cold aperture B than it would do were that surface parallel to B. This principle is utilised in the receiver previously described.

Method of Electrical Winding.—It was desired to attain a temperature of at least 1000-1100° C., and for this purpose platinum strip was used. Experiments seem to show that alumina is not the ideal material for the crucible, on account of the fact that in the earlier experiments the platinum winding invariably broke down on cooling after maintaining the radiator for some hours at 1000° C., and after switching off the heating current. It

^{* &}quot;A Determination of the Radiation Constant," 'Roy. Soc. Proc.,' A, vol. 88, p. 49 (1913).

appeared that the platinum adhered to the crucible, and on cooling the expansion of the alumina fractured the platinum strip. In view of this property of the clays at high temperatures it is probable that porcelain would be preferable.

It was desirable that the strip should be held in position in some manner,



F10. 1.

particularly on the cones. The dental cements tried for this purpose proved to be unsatisfactory—breakdowns continued to occur, and on examination the strip seemed to show that electrolysis was taking place with the cement. The two main difficulties to be overcome were (1) the expansion of the crucible on cooling, (2) electrolysis.

The first was solved by "crimping" the platinum strip between two cog-

wheels, and winding it so as to be separated from the crucible by a pliable mica bed. This prevented the strip adhering to the crucible and allowed of considerable movement. The electrolysis difficulty was overcome by removing all traces of dental cement and replacing it by pure aluminium oxide. Since the adoption of this method of winding no further difficulty has been experienced. These practical points are recorded as they may be of interest to others concerned in high temperature furnace work.

Some 30 metres of platinum strip 0.42 cm. wide and 0.012 cm. thick were used. This thickness was chosen for strength to minimise the risk of mechanical fracture. Before winding, the whole crucible was encased in mica to prevent the strip adhering to the alumina.

Winding the Cylinder.—The crimped platinum strip was wound over the mica jacket of the alumina cylinder with a spacing of approximately 1 cm. between the windings. The platinum was now interlaced with narrow mica strips to keep it in position and so prevent short-circuiting. This was covered with another mica jacket to prevent contact between the conductor and the kieselguhr. Although mica provides an excellent insulating medium which is chemically inactive, it becomes friable and powdery at 1000° C., and it was therefore necessary to provide an additional strengthening jacket which remains hard at high temperatures. This was attained by covering the whole with pure asbestos cloth and pasting the outside of this with asbestos cement. Fig. 2 shows the winding in section. On examination this was found to be in very good condition both mechanically and electrically after running on several occasions at 1100° C.

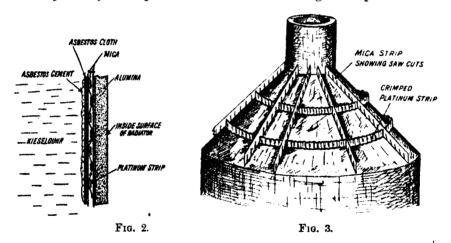
Winding the Cones.—Owing to the stiffness of the platinum strip it was impossible to make it lie flat on the conical surface. Further, some means had to be devised whereby the strip could be held in position during the process of winding and the spacing maintained during the heating so that there was no possibility of short-circuiting. The platinum strip was formed into a conical cage using stout mice strip as the spacing and supporting material. Equally spaced saw cuts were made in the mica, these served to grip the platinum and give the necessary spacing. The principle of the arrangement is shown in fig. 3. Two platinum coils and a few of the mica strips are illustrated on an enlarged scale. A strengthening matrix was provided by pouring into the interspaces a thick paste of pure aluminium oxide and water. The water was driven off by heating electrically, leaving a compact mass giving excellent insulation and support.

The ends of the platinum winding were brought out through the kieselguhr and connected to a row of six binding screws on the outside of the case. For the purpose of economy, heavy copper leads were used; but, owing to oxidation

of the copper-platinum joint at this high temperature, the copper had to be discarded. To avoid further difficulty, the platinum strip was made continuous to the binding screws, so that the only "contact" in the circuit was cool and visible.

Supporting and Lagging the Crucible.—The crucible was supported by means of two blocks of alumina which rested in the collars of the two circular end castings, as shown in fig. 1. These castings were rigidly attached to each other by means of a steel cylindrical jacket, the intervening spaces being filled with kieselguhr. The apparatus rested on a V-block casting and weighed approximately 130 kgm. A covered "hand-hole" was cut in the steel cylinder to facilitate the removal of moisture when drying out and also the examination of the interior when necessary.

Arrangements for Temperature Measurement.—Owing to the possible incon-



venience in introducing a thermocouple through the aperture B (fig. 1) during radiation measurements, a side hole was provided as shown. The direction of this inlet allowed of the couple being moved parallel to the radiating surface and any differences of temperature determined. Further, the position of the hole is such that it will not be "visible" from the aperture of the receiving apparatus to be used in future experiments.

The temperature was measured by a platinum platinum-rhodium thermocouple which had been calibrated at the National Physical Laboratory for the earlier experiments on the radiation constant. The temperature was observed by means of the deflection of a calibrated moving-coil galvanometer. This method is of sufficient accuracy for the present purpose of obtaining uniformity, since an absolute value of the temperature is not required.

,,

In order to determine whether the galvanometer was indicating temperatures of the right order, a modification of the "hot-wire" method was used to check the indications of the thermocouple. While the furnace was slowly heating up, an additional couple of nickel-nichrome, joined by a short silver wire, was inserted and connected to a galvanometer, which served to indicate the time at which the silver melted. At this instant the scale reading of the Pt-PtRh couple was observed and was found to agree with the melting point of silver (961° C.) to within a few degrees.

Adjustment of the Heating Current to give a Uniform Temperature .-

Let the winding on the back cone A = Circuit 1.

- " cylinder = Circuit 2.
- " front cone = Circuit 3.

The resistances of the three circuits were measured at room temperature. Since the heat insulation of each of the three sections is not equally efficient, then it is obvious that an equal consumption of energy in each circuit will not provide a uniform temperature within the enclosure. The simplest plan is to allow each winding to act as its own thermometer by arranging that the increase in resistance is in the same ratio in each case. Usually the three circuits were put in series and a suitable current left running overnight. When the temperature reached 700–800° C. the circuits were arranged in parallel, so that the energy consumption of each could be controlled and measured from time to time. At 1100° C., the temperature at which uniformity was required, the energy consumed in each circuit was measured and then so adjusted that the resistance of each coil had increased in the same ratio. As will be seen later, this gave the required conditions. The following is characteristic of a set of observations:—

Let C_1V_1 , C_2V_2 , C_3V_3 , represent the current and potential for circuits 1, 2, and 3 respectively.

		Resist. at 1100° C. Resist. at 12° C.	Energy consumption in watts.	Total energy consumption.
Circuit 1 {	$C_1 = 9.0 \text{ amps.}$ $V_1 = 70.0 \text{ volts}$	4 ·2(0)	630	
Circuit 2 {	$C_2 = 6.9 \text{ amps.}$ $V_2 = 67.9 \text{ volts}$	} 4.2(0)	468	1743 watta
Circuit 8 {	$C_3 = 8.7$ amps. $V_3 = 74.0$ volts.	4 ·2(0)	645	J

Temperature = 1150° C.

Assuming the previously determined value of the radiation constant $= 5.89 \times 10^{-5}$ ergs/sec. cm.² deg.⁴, the rate of emission of energy through the aperture B at 1100° C.

= 508 watts.

"Efficiency" =
$$\frac{\text{Energy appearing as radiation from aperture}}{\text{Total energy consumption}} = \frac{508}{1743}$$

= 0.29,

that is to say 29 per cent. of the energy put in appears as radiation. Making a similar calculation for the Herœus furnace used in the earlier experiments and assuming that it emits full radiation it can be shown that the "efficiency" in this case is only about 25 per cent.

Note.—The energy was supplied by a direct current machine capable of giving 50 amperes at any potential from 20 to 160 volts. By this means the potential could be varied and the necessity for resistances variable over large ranges avoided. One small variable resistance in each circuit was provided and adjusted such that the machine was running at 110 volts when the temperature required was obtained. To avoid fluctuations in the dynamo potential the machine was now switched in parallel with the departmental 110 volt battery. When perfectly steady conditions of temperature were desired the machine was thrown out of circuit, leaving the radiator running off the battery alone. The electrical connections are shown in fig. 4.

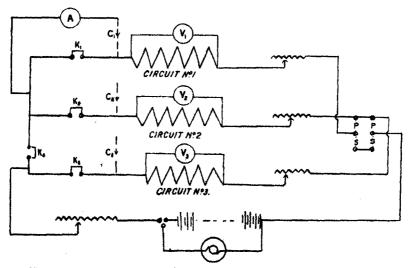
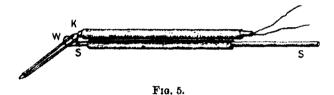


Fig. 4.—Electrical connections for constant-temperature enclosure. For "parallel" close PP and K4. For "series" close SS and open K4.

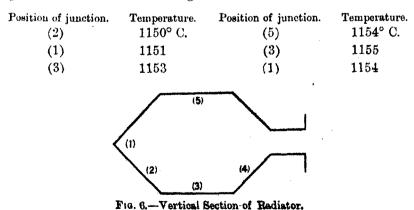
follows :---

Exploration of Temperature Distribution.—This was most conveniently carried out by inserting the thermocouple through the aperture B. In order to place the junction at different points within the radiator the length of the couple immersed must vary if used in the ordinary way. Unless the wires of the couple are chemically pure and physically uniform the electromotive force will depend upon the length immersed. It was known from previous investigation that the couple used was defective in this respect. It was therefore necessary to devise some means of reaching different parts of the radiator, keeping the length of the couple immersed constant. The couple was insulated by means of twin-bore fireclay tubing which was supported in a porcelain tube so that the break K in the twin fireclay (see fig. 5) was



approximately at the centre of the enclosure. Another porcelain tube was attached alongside and carried a loosely fitting fused silica tube provided with a platinum wire loop W. This loop encircled the loose end of the thermocouple so that the junction could be brought to any position within the enclosure by sliding the silica tube S in its porcelain guide. In this manner the temperature distribution was determined. For the values of the energy consumption given above the temperatures at the various points were as

A series of observations of the temperature at the various positions shown in fig. 6 were taken in the following order:—



It will be seen that the temperature was rising.

After waiting for steadier conditions the following series were taken:—

Position of junction. (3)	Temperature. 1149° C.	Position of junction. (3)	Temperature. 1150° C.
(4)	1147	(1)	1149
(1)	1149	(4)	1150

There is evidence here of a slight rise of temperature and the maximum difference of 3°C, occurs at the same place (position 4). It is quite useless to attempt further refinements at the present stage, since it is intended to determine the radiation constant for various temperature distributions within the enclosure. The results so obtained will determine the degree of uniformity which is necessary. If for instance the temperature of the cone opposite A is reduced by 100°C, and the value of the radiation constant obtained remained unaltered then the uniformity described above is sufficiently good. For this reason it is proposed to proceed with the radiation experiment without further delay.

The Quality of the Radiation emitted.—There is no satisfactory means of determining the diffusing power of a sample of the alumina at the temperature of the radiator (1100° C.), owing to the difficulty of obtaining the actual temperature of the radiating surface of an exposed sample. It is highly probable that a porous clay is an exceedingly good radiator on account of the pores providing a surface of minute full radiators. Such was the surface of the crucible. As a further precaution this surface was covered with a dull black coating (by Messrs. Morgan, of Battersea, London, S.W.) which would withstand 1100° C.

My colleague, Dr. Guy Barlow, has shown that the radiation passing through a circular aperture of area α in a spherical uniform temperature cavity of cross-section A departs from the full radiation at that temperature by approximately $\alpha R/A$ per cent., where R is the percentage of the radiation diffusely reflected by the material.

If we assume that the black alumina surface diffusely reflects as much as 5 per cent., then the radiation from the aperture B departs from the full radiation at that temperature by only about 0.2 per cent.

I am indebted to the late Prof. J. H. Poynting, F.R.S., for granting the funds which enabled me to carry out this investigation, and also to Mr. G. O. Harrison, of the Physics Workshop, for the valuable assistance he has rendered.

On the Spectra of Ordinary Lead and Lead of Radioactive Origin.

By Thomas R. Merton, B.Sc. (Oxon.).

(Communicated by A. Fowler, F.R.S. Received December 21, 1914.)

The view that the spectra of isotopes are identical was first put to the test by Russell and Rossi* and Exner and Haschek,† who examined the spectra of thorium and ionium preparations. The former of these observers worked with a mixture containing at least 10 per cent. of ionium, but no lines were found which were not present in the spectrum of pure thoria.

Aston; has submitted meon to fractional diffusion, by which a spartial separation was effected, as shown by the change of density, but no change in the spectrum was observed.

More recently Soddy and Hyman§ and Richards and Lembert have compared the spectrum of lead of radioactive origin with that of ordinary lead. The former of these investigators, who worked with lead from thorite, found that the line $\lambda=4760\cdot 1$ was stronger in ordinary lead han in the thorite lead, but that the spectra in other respects appeared to be identical. Richards and Lembert also found that the spectra were identical. In both of these investigations, the Féry spectrograph was used for the photography of the spectra; no details are given, but it is presumed that in both cases the spectra of the radioactive and ordinary lead were photographed in juxtaposition on the same plate.

This method is admirably suited to a general comparison, but it gives no numerical data as to the exact degree of identity of the wave-lengths in the two spectra.

It might reasonably be expected that in the spectra of isotopes small differences of wave-length would occur, though the character and distribution of the lines were the same.

According to the recent views of Prof. Hicks, an atomic weight term enters exactly into the separations of doublets and triplets in series spectra. No series have yet been found for the spectrum of lead, but Kayser and Runge¶

^{* &#}x27;Roy. Soc. Proc.,' vol. 87, p. 478 (1912).

^{† *}Sitzungsber, K. Akad. Wiss. Wien, vol. 121 (2 Abth.), p. 175 (1912).

¹ British Association Meeting, 1913.

^{§ &#}x27;Chem. Soc. Trans.,' vol. 105, p. 1402 (1914).

^{|| &#}x27;Amer. Chem. Soc. Journ.,' vol. 36, p. 1329 (1914).

^{¶ &#}x27;Wied. Ann.,' vol. 52, p. 93 (1894).

have found that a group of ten lines repeats itself three times with constant frequency differences. It seems probable, however, that doublet or triplet series exist in the lead spectrum, and for the lines which fall into such series there should, according to the views of Prof. Hicks, be differences of wavelength in the two isotopes corresponding with the difference of atomic weight.

In the present investigation, I have made a comparison of the wave-lengths of some of the most prominent lines in the spectrum of ordinary lead and of the lead in Joachimsthal pitchblends. The spectra were photographed with a concave grating spectrograph, mounted according to the arrangement of Eagle* and provided with a concave grating of 4 feet radius of curvature having 20,000 lines to the inch. The plates were measured on a Hilger micrometer.

The spectra were produced in the carbon arc, the carbons being cored, as the case might be, with the pitchblende residues or with iron oxide containing a small proportion of ordinary lead. The residues contained a considerable quantity of iron which served as a comparison spectrum. A number of plates were taken, in which the two spectra were in juxtaposition, and the lines due to lead were found to be identical in the two spectra.

The object of the present investigation, however, is to set some superior limit to any wave-length differences that might occur.

The wave-lengths of the principal lead lines between $\lambda = 3500$ and $\lambda = 4100$ have therefore been independently measured in the ordinary and radioactive lead spectra, the iron lines being used as standards. The values obtained are given in the following table:—

λ, ordinary lead.	λ, lead from residues.	λ, ordinary lead— λ, lead from residues.	λ, Кау вег
*8572 -88	8572 .88	±0.00	8572 -88
8639 ·72	8689 ·69	+0.08	8689 .71
*3671 .66	3671 -64	+0.02	8671 .65
3688 -59	3683 -60	-0.01	3688 -60
*8740 ·08	3740 06	+0.02	8740 .10
4057 98	4057 .99	-0.01	4057 97
4062 .31	4062 .83	-0.02	4062 30

The dispersion was about 10 Å.U. per millimetre and the differences observed, which are not systematic, are within the experimental error, and it may therefore be concluded that no differences greater than 03 Å.U. occur in these lines. The three lines marked with an asterisk are members of the groups of ten, discovered by Kayser and Runge (loc. cit.).

^{* &#}x27;Astrophys. Journ.,' vol. 31, 2, p. 120 (1910).

The atomic weight determinations of Richards and Lembert (loc. cit.), Honigschmid and Horovitz* and Curie† show that the atomic weight of lead from the pitchblende residues is somewhat greater than the value predicted by theory, this being no doubt due to the presence of a small quantity of ordinary lead in the pitchblende. If the spectrum lines in the two leads differed in wave-length by a small amount, the lines from the pitchblende residues would be double. If the components were not resolved in the spectroscope, the doubling should nevertheless make itself felt as an apparent shift or an asymmetric broadening of the line. On the assumption that the lead in my residues has an atomic weight about 5 unit less than ordinary lead, Prof. J. W. Nicholson has very kindly calculated for me the order of the change of wave-length to be expected according to Prof. Hicks' theory, in the case of lines belonging to series, doublets or triplets.

If the separation of two such lines in a doublet were 50 Å.U. at $\lambda = 4000$ Å.U. (an order of separation which might reasonably be expected to occur in the case of lead doublets), then a change of atomic weight of 0.5 unit should alter the separation of the lines by about 0.3 Å.U., or if each of the lines were shifted by an equal amount, a change of wave-length of the order of 0.15 Å.U. in each line would result.

It may be stated with certainty that in the lead lines, which are not given in the above list but which were observed in the photographs of the spectra taken in juxtaposition, no change of wave-length of this order occurs.

A special examination has been made of the line $\lambda = 4058$. This line is by far the strongest line which can be photographed through glass lenses and The comparison has been made of this line in the two lead spectra by photographing the ring systems produced by means of a Fabry and Perot étalon. The line $\lambda = 4058$, when produced in the carbon arc at atmospheric pressure, is too broad for the production of interference rings of sufficiently good definition. The spectrum was therefore produced in a glass globe of about 1 litre in capacity, exhausted by means of a Fleuss pump to a pressure of a few millimetres of mercury, between carbon rods, cored with small quantities of the two leads as carbonates or oxides. Under these conditions sharp definition could be obtained. The convergent beam of light from a lens placed at a suitable distance from the arc-passed through the étalon, and an achromatic lens of 6 inches focal length brought the ring system to a focus on the slit of a large Hilger constant-deviation spectroscope provided with a camera attachment. The étalon consisted of two half-silvered plane parallel glass plates separated by three glass studs, the distance between the

^{* &#}x27;Comptes Rendus,' vol. 158, p. 1796 (1914).

^{† &#}x27;Comptes Rendus,' vol. 158, p. 1676 (1914).

plates being 6.50 mm. The exposures were made within two or three minutes of one another, to avoid variations due to changes of temperature.

Photographs taken in this way showed that the interference rings are identical for the two lead spectra, and measurements of the diameters of the rings agree within the limits of experimental error, the calculated results showing that there is certainly no difference of wave-length for the line $\lambda = 4058$ as great as 0.003 Å.U. in the spectrum of ordinary lead and of the lead from pitchblende.

In conclusion, I should like to thank Prof. Nicholson for the calculation which he has made for me.

On the Viscosity of the Vapour of Iodine.

By A. O. RANKINE, D.Sc., Fellow of and Assistant in the Department of Physics in University College, London.

(Communicated by Prof. A. W. Porter, F.R.S. Received January 15, 1915.)

In a previous communication. I have described the measurements I have made of the viscosity of bromine vapour. The method used for this purpose involved the distillation of bromine from one vessel to another through a capillary tube. The pressure difference between the two ends of the capillary was established by maintaining the two vessels at suitable different temperatures, and the rate of transpiration of the bromine vapour was estimated by observing the volume of the liquid bromine which evaporated in a given time. It was hoped that the same method could be applied to iodine by adjusting the temperatures of evaporation and condensation to values above the melting point of iodine (113° C.), and measuring the transpiration rate by means of the disappearance of liquid from the evaporation vessel.

Preliminary experiments, however, soon revealed the fact that the liquid iodine was not sufficiently mobile, and its surface was too indefinite and variable in shape to allow small changes of volume to be observed. It was, therefore, found necessary to modify in several respects the method used with bromine.

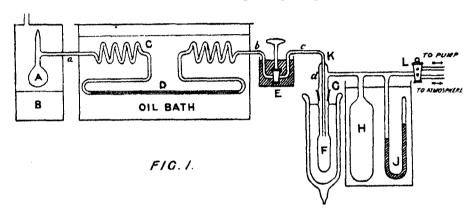
The present paper describes the modified method, which was found to work extremely well and to give very consistent results. Values of the viscosity of

^{* &#}x27;Roy. Soc. Proc.,' A, vol. 88, pp. 575-588 (1913).

gaseous iodine have been obtained at four different temperatures ranging from 124° C. to 247° C.

Description of Apparatus.

The details of the apparatus used are shown in fig. 1, which is not drawn to scale but intended merely to illustrate the principle of the method.



The iodine, in a solid state, is contained in the bulb A, which is connected by means of ordinary quill glass tubing to the spiral C, and thence to the straight capillary tube D. The other end of the capillary tube is similarly connected through another spiral to the special tap E, the latter being so arranged that it can be immersed in a bath of mercury. From the other side of the tap the tubing leads to the re-entrant joint K. The outer tube is connected by a conical joint at G to a tube F, which can be removed when desired. The apparatus is further connected, as shown, to the large bulb H, and the mercury gauge J, and finally to the two-way tap L, by means of which the apparatus can be connected to a Toepler pump or the atmosphere; or the tap may be kept closed.

The bulb A is surrounded by a water boiler B so that its temperature may be kept at the temperature of boiling water. An oil bath suitable for temperatures up to 250° C, surrounds the spirals and capillary. The removable tube F is immersed in a freezing mixture contained in a vacuum vessel, and a water-bath surrounds the bulb H and the mercury gauge. Exposed portions of the apparatus, viz., a, b, c, and d, are wound with spirals of platinoid wire and well lagged with asbestos paper, so that they can be kept at the desired temperature by passing an electric current through the wire.

Principle of the Method.

The saturation vapour pressure of iodine at 100° C. is equal to 4:48 cm. of mercury. If, therefore, having first evacuated the apparatus, we raise the temperature of the bulb A to 100° C, the iodine vapour will be driven through the capillary tube D and ultimately be condensed in the tube F. (This, however, will only be the case provided that all parts of the apparatus between A and F are maintained at temperatures in excess of 100° C., for otherwise condensation may occur elsewhere than in F.) The pressure in F will be practically zero, for the vapour pressure of iodine at the temperature of the freezing mixture (about -20° C.) is neglibly small. transpiration formula is almost certainly not valid in the case where the pressure on one side of the capillary is very small, hence it was deemed necessary to establish a finite and measurable pressure by means of air. The distillation above described would still proceed (although more slowly) if the pressure of air in F is less than the vapour pressure in A. In practice, an air pressure of some 2 cm. of mercury has been used, and this pressure could be measured by means of the gauge J, which is in such a position as to avoid becoming fouled by the iodine.

It will now be seen how the data necessary for the calculation of the viscosity of the iodine vapour can be obtained. The pressure in A is originally the saturation pressure of iodine vapour at the temperature of boiling water at the time of the experiment. Owing to the large surface presented by the iodine—which is solid at 100° C.—it is probable that the vapour maintains its pressure at the saturation value, in spite of the fact that it is being continually removed through the capillary. The pressure on the other side of the capillary is that observed by means of the gauge. By weighing the removable tube F before and after an experiment, the mass of iodine transpired in a given time can be determined. These data, together with the dimensions of the capillary tube, can then be used to calculate the viscosity.

Details of Experiment.

The method of carrying out an experiment was as follows:---

The tube F was first of all accurately weighed and then refitted in position with the freezing mixture surrounding it. With the tap E open, the whole apparatus was then evacuated, the bulb A being meanwhile at atmospheric temperature, at which iodine has a vapour pressure of not more than a small fraction of a millimetre. The tap E was then closed, and dry air was admitted into the part of the apparatus between E and L until the pressure was about 2 cm. of mercury. By immersing the large bulb H in water at ordinary

temperature this pressure was kept remarkably steady. An electric current was then switched on through the coils surrounding a, b, c, and d, the current being of such a value as to maintain the tubes at about 120° C. The mercury bath surrounding the tap E was also heated to and kept as nearly as possible at this temperature throughout the experiment. It may be mentioned incidentally that though the behaviour of the tap E at this high temperature was expected to give trouble, it was found to work exceedingly well. The tap was lubricated with ordinary black lead to which a small trace of tallow had been added. In these circumstances it was found to be quite gas tight and thoroughly reliable.

The oil bath was heated by means of gas burners to the temperature at which it was desired to measure the viscosity, and the gas supply adjusted until the temperature was steady. A paddle-wheel rotated by means of a motor (not shown in the diagram) was used for continually stirring the oil in the bath. Finally the water in the boiler B was boiled, and the apparatus was then ready for beginning the measurement.

It will be well, at this stage, to consider the conditions of the gases in the various parts of the apparatus. On the left-hand side of the tap E the apparatus contains nothing but iodine. The coolest place is the bulb A, which contains the solid iodine, and the temperature of which is about 100° C. In the apparatus, from A to E, the pressure of the iodine vapour is equal to the saturation pressure at the temperature of A, i.e. about 4.5 cm. In the part of the apparatus within the boiler B the vapour is saturated, elsewhere it is superheated, the temperature being considerably higher than the boiling point of water.

On the right-hand side of the tap E there is at first air only, the pressure being about 2 cm. On opening the tap iodine vapour will pass through it, displace the air in C, but rapidly condense in the unheated portion of the apparatus. The flow of vapour through the capillary, and its subsequent condensation in F, continues so long as the tap E is kept open, and provided that the solid iodine evaporates in A rapidly enough to keep the pressure in excess of the air-pressure which has been established in H.

During an experiment the tap E was opened at a definite moment, and left open for a measured time. Meanwhile observations of the pressure in H were taken by means of the gauge, but in none of the experiments could any change be observed. At the end of the experiment E was closed, and air at atmospheric pressure was admitted into the apparatus through L. The tube F was then removed and weighed; whence, by subtracting the previous weight, the mass of iodine condensed in F was determined.

In order to eliminate a small but appreciable error due to the iodine which

at the beginning of the experiment filled the tube between the capillary and the tap E, two separate determinations were made, one usually lasting for 10 minutes and the other for 80 minutes. The difference between the two masses condensed in F then gives the amount which had passed through the capillary in 70 minutes.

The question also arises as to whether the pressure in the bulb A retains the saturation value during the progress of the transpiration. This bulb has a considerable volume unoccupied by solid iodine. It therefore contains, previously to opening the tap E, a considerable supply of iodine vapour at the saturation pressure. If, however, after opening the tap, evaporation is not sufficiently rapid to maintain saturation, the pressure would gradually fall, and consequently the rate of transpiration would diminish.

Experiments which extended over various periods of time showed no such diminution, and one may therefore conclude that the powdered iodine supplies a sufficiently large surface to keep the pressure at the saturation value.

Calculation of Results.

As shown in a previous communication,* Meyer's transpiration formula, when transformed so as to apply to mass transpired instead of volume transpired, takes the form—

$$\eta = \frac{\pi R^4}{16l} \cdot \frac{(p_1^2 - p_2^2) t}{p_0 m} \rho_0 \frac{T_0}{T},$$

where η is the coefficient of viscosity, R the radius and l the length of the capillary tube, p_1 and p_2 the pressures of entry and exit, m the mass transpired in time l, ρ_0 the density of the gas at the pressure p_0 and temperature T_0 , and T the absolute temperature of the gas during transpiration.

This equation assumes that the vapour behaves like a perfect gas, which, at the high temperatures and under the low pressures of the experiments, is approximately true. The value of ρ_0 , the density which iodine vapour would have at the normal temperature and pressure if it behaved like a perfect gas under those conditions, has been calculated from its molecular weight as 0.01133 grm. per cm.³.

The same capillary tube was used as in bromine measurements and the value of $l/R^4 = 3.763 \times 10^8$ cm.⁻⁸ at 13° C.

The pressure of entry p_1 is the saturation pressure of iodine vapour at the temperature of boiling water. This was obtained by interpolation from the observations of Ramsay and Young, \dagger the temperature of boiling being calculated

^{* &#}x27;Roy. Soc. Proc.,' A, vol. 88, p. 580.

[†] Ramsay and Young, 'Chem. Soc. Journ.,' vol. 49, p. 453 (1886).

from the barometer reading. The values vary from 4.247 cm. at 99° C. to 4.729 cm. at 101° C.

The pressure of exit p_2 was observed directly by means of the gauge, subject to the small temperature correction.

Corrections were applied to the approximate value of the viscosity calculated from the above equation, firstly for the variation of the dimensions of the capillary tube with temperature, and secondly for the slipping of the gas over its internal walls. In the first case the coefficient of cubical expansion of glass was taken as 0.00003 and the correction at the highest temperature, 247° C., amounted to 0.7 per cent. The second correction amounts to multiplying the approximate viscosity by the factor $1+4\lambda/R$, where R is the radius of the capillary and λ the mean free path of the gas molecules under the conditions of the experiment. The value of λ , which is only required approximately, was calculated from the approximate value of the viscosity, using the customary formula based on the kinetic theory. At the highest temperature this correction amounted to 2.9 per cent.

The results of the various experiments and the data from which they are calculated are given in the following Table:—

Table I.

Temperature in degrees Centigrade.	in centimetres of mercury.	in centimetres of mercury.	Transpiration rate in grm./sec. × 10°.	Approximate viscosity × 104.	Corrected viscosity × 10 ⁴ .
124 0	4 .588	2 · 251	6 ·158	1 .801	1 .648
124 0	4 · 478	2 .234	5 .952	1 .801	1 843
170 •0	4 '546	2 .260	5 .028	1 .979	2 .083
170 0	4 435	2 219	4 .738	1.990 .	2 044
205 ·4	4 .388	2 ·199	4.008	2 ·131	2 ·199
205 ·8	4 '580	2 ·276	4 ·269	2 · 129	2 ·197
247 .0	4.524	2 276	8 .598	2 .818	2 .401
247 -2	4.562	2 288	3 .679	2 .310	2 898

The next Table shows the collected mean results, which may be taken as reliable to within one unit in the third significant figure.

Table II.

Temperature.	Viscosity in C.G.S. unit × 104.		
124 0	1 .842		
170.0	2 .038		
205 -4	2 ·198		
247 ·1	2 · 397		

Discussion of Results.

The first point of interest in connection with these results is to deduce from them the value of Sutherland's constant C in his equation*

$$\eta = K \frac{T^{\dagger}}{1 + C/T},$$

where T is the absolute temperature and K another constant.

If we base the calculation upon the values of the viscosity at the two highest temperatures we obtain C=590. The reason for excluding the lower temperatures is that Sutherland does not claim that his law is valid for a vapour near the point of saturation. Nevertheless, the value C=590 gives a calculated value of the viscosity at 170° C. differing very little from the observed value, although at the lowest temperature, at which the vapour was superheated to the extent of 24° C. only, there is a notable difference in the same sense as has previously been shown to exist for bromine.

This is shown in the following Table:-

Temperature. Viscosity observed × 10⁴. Viscosity calculated × 10⁴.

124 1 84 1 80
170 2 04 2 03
205 4 2 20 2 20
247 1 2 40 2 40

Table III.

We may now test how far the results for iodine fall into line with the empirical laws which I have shown to hold for bromine and chlorine.

The critical temperature of iodine is 507° C.,† or 780° absolute. The ratio T_c/C is therefore 780/590 = 1.32. This compares with 1.28 for the same ratio in the case of chlorine and 1.25 for bromine. Considering the difficulties of obtaining accurately the critical temperatures of these gases, and also the value of Sutherland's constant C, these three ratios are equal within the accuracy of the experiments.

Further, if we calculate by extrapolation of Sutherland's equation the viscosity of iodine vapour at the critical temperature, we obtain the value $\eta_c = 3.58 \times 10^{-4}$, and the value of η_c^2/A , where A is the atomic weight, is 1.01×10^{-9} , which is practically equal to the same ratio for chlorine and bromine.

^{* &#}x27;Phil. Mag.,' vol. 36, p. 507 (1893).

[†] From Landolt and Börnstein's Tables.

A consideration of the following Table will show to what degree of accuracy these two empirical laws hold:—

Table IV.

Gus.	. T./C.	,10° η _ε 2/A.
Chlorine	1 ·28 1 ·25 1 ·32	1 ·02 1 ·03 1 ·01

It will be seen that this group of gases in the periodic Table obey laws similar to those which hold for the inert gases.*

A New Type of Series in the Band Spectrum Associated with Helium.

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(Received January 19, 1915.)

Introductory.

A previously unknown band spectrum was noticed in the course of experiments on hydrogen and helium made at the Imperial College in 1912, and was further investigated and described by W. E. Curtis in the year following.† An independent account of this spectrum was also given, almost at the same time, by Dr. E. Goldstein.‡ In each case, some hesitation was felt in attributing the new spectrum solely to helium, in consequence of the persistence of traces of hydrogen in the helium tubes employed.

Mr. Curtis found that the band spectrum was best developed, in the wider parts of the tubes, when a discharge with small capacity and a small air-gap was passed through helium at a pressure rather higher than that which is usual in sealed tubes of the gas. The discharge is then quite brilliant, and by giving long exposures, amounting in some cases to seven or eight hours,

^{* &#}x27;Phil. Mag.,' January, 1911, p. 45.

^{† &#}x27;Roy. Soc. Proc.,' A, vol. 89, p. 146 (1913).

^{† &#}x27;Verh. d. Deutsch. Phys. Gesell.,' vol. 15, p. 402 (1913).

Mr. Curtis obtained an excellent series of photographs of the spectrum with the concave grating of 10 feet radius, some of which were in the second and third orders. Photographs with other instruments were also taken by Mr. Curtis, but he has been unable to continue the investigation in consequence of his temporary enlistment. Under these circumstances it has been thought desirable to make a preliminary analysis of the bands, so that attention might be drawn to any points of special interest without undue delay.

As previously described and illustrated by Curtis and Goldstein, the spectrum includes some conspicuous bands with single heads, others with double heads, and a number of complex regions in which no heads are recognisable at sight. A prominent fluting with a single head, beginning at λ 5733, degrades to the violet, but otherwise all the flutings which have been recognised as such are degraded to the red.

The first result of the investigation was the unexpected discovery that the double-headed bands are not arranged according to the usual law of band spectra, but closely follow the law of line series. The structure of the individual bands, however, is essentially the same as that of bands which are distributed in the more usual way; that is, the distances between successive lines of a series form an approximately arithmetical progression. Mr. Curtis's plates show five bands of the main doublet series, and four additional bands in the ultra-violet which plainly belong to it have since been photographed on a small scale.

A fairly conspicuous doublet in the green, $\lambda\lambda$ 5133, 5108, was not included in the main series, and it therefore became important to search for additional bands, in order to determine if there were other series which might be related to the first. Only one other doublet, a faint one at 3634, 3625, was at first recognised by inspection, and it remained to be seen if others could be picked out in the more complex regions where bands of different types might be superposed. For this purpose, all the individual lines composing the bands between λ 6500 and λ 3347 were measured, so that the special characteristics of the different types of bands could be ascertained. About 1300 lines in all have been measured, but the final determinations of the wavelengths, with the necessary corrections for temperature and other sources of error, will occupy a great deal of time, and it is not considered desirable to give so long a list until the wave-lengths have been freed from systematic errors. The provisional wave-lengths, however, are adequate for a first discussion.

As a general statement, it may be remarked that the lines composing the single-headed bands show a smaller second difference than those belonging

to the doublets, but in each case the second difference increases in passing from bands in the red to those in the violet part of the spectrum. A great many of the band lines can be arranged in series, but comparatively few additional heads have been traced or suspected. Two doublets which are related to those about 5133 and 3634, however, have been identified, and also a few single-headed bands in addition to those tabulated by Curtis. No regularity in the arrangement of the single bands has yet been recognised, and the present paper is accordingly restricted to the consideration of the doublets.

Structure of the Doublets.

The structure of the strongest double band, at $\lambda\lambda$ 4648, 4625, is illustrated in fig. 1, where the intensities of the component lines are represented roughly by the lengths of the lines in the diagram. In this case, the more refrangible, and weaker, component of the doublet includes seven strong lines, and the less refrangible component at least eight. In each case the lines converge to the observed heads. The "tail" of the band consists of a large number of lines, of which the brightest form the obvious series which is shown in the diagram; the calculated convergence point of

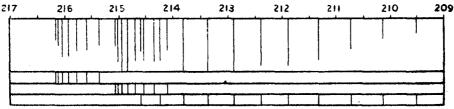


Fig. 1.—The Doublet Band λλ 4648, 4625. (The scale is that of wave-numbers, and only the chief lines are shown,)

this series lies considerably on the violet side of the two observed heads, and the lines cease to be visible before the convergence point is reached. Series of the latter type are very numerous throughout the spectrum; they appear to accompany all the bands, whether single or double, and the second difference is apparently dependent on that in the band with which it is connected.

The provisional wave-lengths of the lines mapped in fig. 1 are given in Table I, which also shows the corresponding wave-numbers (reduced to vacuum), and the first and second differences. It will be seen that the second differences are approximately constant.

Intensity.	Wave-length (I.A.).	Wave-number.	1st difference.	2nd difference.	Remarks.
4 5 7 7 6 6 5	4625 ·43 26 ·12 27 ·54 29 ·98 38 ·25 87 ·32 42 ·37	21613 ·7 10 ·5 03 ·8 21592 ·5 77 ·2 58 ·3 84 ·8	3 · 2 6 · 7 11 · 3 15 · 3 18 · 9 28 · 5	3 · 5 4 · 6 4 · 0 8 · 6 4 · 6	More refrangible head.
.5 8 10 10 8 8 8	4648 · 52 49 · 38 51 · 01 53 · 37 56 · 35 60 · 06 64 · 48 69 · 58	21508 *8 02 *3 21494 *8 83 *9 70 ·2 53 ·1 32 ·7 09 ·3	4·0 7·5 10·9 18·7 17·1* 20·4 23·4	3 · 5 3 · 4 2 · 8 3 · 4 3 · 3 3 · 0	Leas refrangible head.
6 8 10 10 10 9 9 8 6 4	4658 ·80 66 ·81 75 ·70 85 ·34 95 ·75 4706 ·82 18 ·61 31 ·04 44 ·18 57 ·69 71 ·86	21458 ·9 22 ·0 21881 ·3 87 ·3 21290 ·0 89 ·9 21186 ·8 31 ·2 21072 ·9 12 ·8 20950 ·4	86 ·9 40 ·7 44 ·0 47 ·8 50 ·1 53 ·1 55 ·6 58 ·3 60 ·1 62 ·4	3·8 3·3 3·3 2·8 3·0 2·5 2·7 1·8 2·3	Chief series in

TABLE I.—Details of the Doublet 4625, 4648.

The Main Series of Doublets.

The bands belonging to the main series of doublets are readily recognised on inspection of the photographs. They all occur in regions which are free from complication by the superposition of other bands, and the last seven are apparently the only bands which occur in the ultra-violet between λ 3450 and λ 2950, beyond which the spectrum has not yet been examined. The intensities of the bands decrease gradually in passing along the series.

The wave-lengths (International scale) and wave-numbers (corrected to vacuum) of the heads of these bands are given in Table II; the first three have been derived from grating plates, but the remainder are only approximate values obtained from photographs taken with much smaller dispersion.*

Calculations soon confirmed the suspicion that the series was of the character hitherto exclusively regarded as belonging to line spectra. The

* The instruments which would ordinarily have been used for improving on the wavelengths are detained in Russia, where they were taken for observations of the total solar eclipse of 1914, August 21.

series may, in fact, be represented in the usual way by the formulæ of Rydberg or Hicks. For the less refrangible components of the doublets, which are the stronger, the following formulæ have been calculated:—

$$n = 34295.86 - \frac{109679.22}{(m+0.928427)^9},\tag{I}$$

$$n = 34295 \cdot 13 - \frac{109679 \cdot 22}{(m + 0.931561 - 0.006100/m)^{2}}.$$
 (II)

The adopted value of the Rydberg constant is that given by Curtis for the International scale, derived from his measurements of lines of hydrogen.* The differences between the observed and calculated wave-numbers are shown under I and II in Table II, and it will be seen that the bands are represented with quite an ordinary degree of accuracy.

The wave-number intervals between the two components of the doublets diminish in passing to the ultra-violet, but the convergence is less rapid than would be the case if they corresponded with the components of doublets in the Principal series of a line spectrum.

Attempts to unite the more refrangible components of the doublets in formulæ have been less successful. The simple Rydberg formula leaves large residuals, and even the Hicks formula with four constants is not entirely satisfactory. The following formulæ have been calculated:—

$$n = 34330\cdot18 - \frac{109679\cdot22}{(m+0\cdot936830)^2},\tag{III}$$

$$n = 34324.725 - \frac{109679.22}{(m+0.960333-0.045747/m)^2},$$
 (IV)

$$n = 34310.966 - \frac{109679.22}{(m+1.051264 - 0.472053/m + 0.495248/m^2)^2}.$$
 (V)

The observed minus calculated values are shown under III, IV, V in Table II, from which it will be seen that there are considerable systematic residuals in each case. A Ritz formula, with three constants, has also been calculated; it gives residuals slightly larger than those given by formula IV.

In view of the observed rate of contraction of the doublets, the limits given by formulæ III and IV appear to be too high as compared with the limit 34295 for the series of less refrangible heads, which is probably not far from correct. From this point of view, the limit given by formula V would seem to be nearly correct, relatively to that of the less refrangible heads. On the other hand, the position of the band in the infra-red corre-

Wave-length (I.A.).	,	7F. 996.		$O-C(\Delta n)$.				
	wave-number.		1.	II.	III.	IV.	٧.	
4648 ·52 4625 ·48	21506 ·8 21613 ·7	2	0.0*	0.0*	0 •0*	0.04	0.0	
3676 ·52 3664 ·99	27192 ·1 27277 ·6	3	+3.2	0.0*	+ 24 ·1	0.0*	0 •0	
8856 :48 8847 :99	29785 ·2 29860 ·8	4	+4.9	+ 2 •6	+ 80 ·3	+ 18 -8	0 .04	
3206 ·4 3200 ·6	81178 ·6 31235 ·1	5	+8.4	+ 2 ·1	+ 16 ·7	+ 7.2	-5.4	
8122 ·7 8118 ·1	32014 · 4 32061 · 7	6	+3.4	+ 2 .7	+10.8	+ 5.9	-2.2	
8071 ·1 8067 ·4	32552 ·9 32591 ·6	7	+1.9	+1.6	+ 2.5	+ 0.6	O 8 -	
3036 ·8 3083 ·4	32920 ·0 32956 ·9	8	0.40*	0.0	0.0*	0.0*	0.04	
8012 ·5 8010 ·2	38185 ·6 38210 ·9	9	+2.4	+ 2 ·5	- 8 -5	- 7·1	-4.4	
2995 ·0 2993 ·0	33379 ·0 33401 ·0	10	+1.2	+1.8	-12 ·2	- 9 9	-5.0	

Table II.—The Main Series of Doublets.

* Used in the calculation of constants.

sponding to m = 1 given by V (n = 8824) is very discordant with that indicated for the less refrangible band by I and II (n = 4803, 4711, respectively), and a closer agreement in this respect is shown by III and IV (n = 5093, 4404, respectively).

The difficulty in finding a satisfactory formula for the more refrangible components is doubtless associated with the unusual character of the doublet separations, which resemble neither Principal nor Subordinate series in the case of line spectra. It may be remarked, however, that some of the known line series are not satisfactorily represented by any of the recognised formulæ.

There is at all events no escape from the conclusion that the doublet bands in question are arranged substantially in the same way as the lines in an ordinary line series.

The Second Series of Doublets.

The first doublet of the second series is quite a conspicuous feature in the green of the visible spectrum, and the third can be recognised without

difficulty on the large scale photographs. The heads of the second band, however, occur among other band lines, and were only identified after measurement of the individual lines; the fourth band is very faint, and prolonged exposures would evidently be required to bring out additional members of this series. The positions of these bands are indicated in Table III.

Wave-length (I.A.).	Wave-number.	m.	$O-C (\Delta n).$		
			VI.	VII.	VIII.
5138 ·84 5108 ·22	19475 ·2 19570 ·9	2	0.0*	0 -0*	0.0*
4002 ·87 3989 ·17	24978 ·3 25060 ·9	3	+0.7	+9.4	0.0*
3684 ·42† 3624 ·91	27507 ·0 27579 ·2	4	+1.1	+7.1	+2.9
3462 ·45 3454 ·94	28878 1 28935 9	5	0.0*	0.0*	0.0*

Table III.—The Second Series of Doublets.

The less refrangible heads of the four observed bands are satisfactorily represented by the following Rydberg formula, as will be seen under VI, Table III:—

$$n = 31956 \cdot 22 - \frac{109679 \cdot 22}{(m + 0.964402)^2}.$$
 (VI)

The more refrangible heads, as in the case of the main series, are not well represented by a Rydberg formula, and it is probable that even the Hicks formula would be unsatisfactory if a greater number of bands were available to test its applicability. The values of O—C under VII and VIII in Table III refer to the following formulæ:

$$n = 32014 \cdot 42 - \frac{109679 \cdot 22}{(m + 0.968866)^3}, \tag{VII}$$

$$n = 32005.665 - \frac{109679.22}{(m + 0.982328 - 0.024835/m)^3}.$$
 (VIII)

Corresponding to m=1, formula VI gives 3534 as the wave-number of the less refrangible component of a possible infra-red member of the series, and formulæ VII and VIII give 3721 and 3382 respectively for the more refrangible head.

^{*} Used in calculation of constants.

[†] The first line of the head falls on a helium line; its position has been estimated from other lines near the head.

Comparison of the Two Series.

It is remarkable that, although the two series of doublets follow the law of line spectra individually, no relation between them corresponding to any which exists between the different members of a system of line series is certainly indicated. The series which has been described as the "main series" of doublets, in consideration of its brightness and extent, would probably correspond with the Principal series in the case of a line spectrum if it had any equivalent. The second series would similarly correspond to one of the subordinate series, and the fact that the first term of the series (m=1) occurs with a positive sign may be taken to indicate that it would be equivalent to a Diffuse series. A third series, which would correspond to the Sharp series in a line spectrum, has not yet been identified. In accordance with well known principles, however, an approximate formula for the Sharp series may be derived from that for the Principal, but neither of two or three additional doublets which have been suspected occupy the positions so calculated.

In a system of line series, as expressed by the Rydberg-Schuster law, the common limit of the Diffuse and Sharp series differs from that of the Principal series by an amount equal to the wave-number of the first Principal line. In the present case the difference between the limits of the two doublet series is about 2340, while the wave-number of the first member of the main series calculated by the formulæ I and II is between 4700 and 4800. The difference appears to be too great to be accounted for by the approximate character of the formulæ employed, and, if so, the two doublet series cannot stand in the relation of Principal and Diffuse series. The same conclusion is suggested by the fact that the less refrangible components of the doublets are strongest in both series.

Thus, although there can be no doubt that the heads of the doublet bands are arranged according to the law of line spectra, other relations shown by the different series of a line system do not appear to hold.

Summary.

The band spectrum associated with helium, as previously described by Curtis and Goldstein, includes bands with single heads and bands with double heads. A preliminary analysis of this spectrum has led to the following conclusions:—

(1) The doublets do not follow the ordinary law of band spectra, but can be arranged in two series of the type hitherto exclusively associated with line spectra, and can be approximately represented by the usual formulæ

involving the Rydberg constant. Nine bands of the main series and four of the fainter second series have been identified.

- (2) The two series may be likened to the Principal and Diffuse series in the case of line spectra, but the usual relation between such series is not certainly indicated, and no equivalent of the Sharp series has yet been traced.
- (3) The doublet separations are not in accordance with those associated with line spectra; they diminish in passing along the series, but do not vanish at the limit.

No regularity in the arrangement of the single bands has been recognised.

The author is indebted to Mr. F. S. Phillips and to Major-General du Gard Gray, C.B., for photographs of the new band spectrum supplementing those previously obtained by Mr. Curtis.

- The Influence of Molecular Constitution and Temperature on Magnetic Susceptibility. Part III.—On the Molecular Field in Diamagnetic Substances.
- By A. E. Oxley, M.A., M.Sc., Coutts Trotter Student, Trinity College, Cambridge, Mackinnon Student of the Royal Society.

(Communicated by Prof. Sir J. J. Thomson, O.M., F.R.S. Received June 24, 1914.)

(Abstract.)

The work is a continuation of that in 'Phil. Trans.,' A, vol. 214, pp. 109-146, which contains Parts I and II.

The suggestion made at the end of Part II, p. 143, that the local molecular field in diamagnetic crystalline substances may be comparable with the ferromagnetic molecular field, has been justified. Estimates of the order of magnitude of this field have been obtained from the following sources:—

(a) The change of specific susceptibility accompanying crystallisation. The extent of this change may be interpreted, on Langevin's theory of diamagnetism, as produced by a local molecular field of the order of intensity 10⁷ gauss, which comes into operation on crystallisation (§ 4). This intense local field distorts the molecules and alters the periods of vibration of the contained electrons. From the nature of the structure which has been postulated for a diamagnetic molecule, this field is of an alternating character, the distance over which it is unidirectional being comparable with the

distance between the molecules. When a substance crystallises, the periods of the vibrating electrons will be changed and the extent of this change is the Zeeman effect of the local molecular field. In general we shall get a simple displacement of the line, corresponding to a particular vibration, and not a doubling. This effect is a consequence of the peculiar structure of the diamagnetic molecule and its magnitude is a measure of the shift of an absorption band owing to crystallisation. (Cf. the pressure-shift of spectrum lines.)

(b) The large value of the natural double refraction of crystalline media, as compared with the artificially induced double refraction in the corresponding liquids when subjected to the largest magnetic field at our disposal.

It is at once seen that the local molecular field must be large compared with the largest field obtainable in the laboratory ($< 10^5$ gauss) in order to account for the augmented double refraction of the crystalline state. The value of the local molecular field deduced is of the order 10^7 gauss (§ 4).

- (c) The potential energy associated with the local molecular field. The intense local molecular field which (a) and (b) disclose implies that the potential energy (magnetic) associated with a diamagnetic crystalline structure is very large. This energy, expressed in thermal units per gramme of the substance, is a measure of the latent heat of fusion (§ 5). The values so obtained are of the right order of magnitude. If, as the fusion point is approached, the molecules assume rotational vibrations, then we should expect that the specific heat of the substance would be abnormally high over such a critical region of temperature. Abundant experimental evidence shows that such is the case.
- (d) The change of volume on crystallisation may be interpreted as a magnetastriction effect of the molecular field, providing this field has an intensity of the order 10⁷ gauss locally.

These results are sufficient to establish the magnitude of the local molecular field in crystalline diamagnetic substances and show that it is of the same order of intensity as the ferro-magnetic molecular field. As stated above, this field in diamagnetics is of an alternating character, the distance over which it is unidirectional being comparable with the distance between the molecules. Nevertheless, it produces a definite distortion in every molecule of the crystalline structure. This is in accordance with the hypothesis of molecular distortion, which forms the starting-point of the present work (see the Introduction to Part I). It is this intense mutual action between the molecules which gives rise to the rigidity of crystalline media. As the molecules will exert different mutual influences in different directions.

according to their particular structure, the rigidity will be greater in some directions than in others. This accounts for the existence of planes of cleavage in crystalline media (§ 5).

The experimental evidence for the change of susceptibility on crystallisation, from which the theory of the molecular field in diamagnetic substances has developed, is contained in Part I. About 25 aromatic substances were investigated altogether, and for these the conclusions stated above hold good in so far as the data for individual cases are obtainable. Aliphatic substances, however, show an almost inappreciable change of susceptibility on crystallisation, and the object of the additional experiments of § 6, together with the "parallelism between the magnetic double refraction of liquids and the change of susceptibility due to crystallisation," developed in § 7, is to show that these conclusions may be extended to diamagnetic crystalline media in general. The extent of the induced magnetic double refraction depends upon the degree of dissymmetry and unsaturation of the molecule. induced double refraction in aliphatics is inappreciable (Cotton and Monton), we may conclude that these factors are small for such substances. In the most favourable cases of unsaturation and dissymmetry the value of $\partial \chi$ amounts to a few per cent. only. It is, therefore, probable that with aliphatic substances the value of $\partial \chi$ would not be detectable, even though the molecular field is comparable with 107 gauss.

The source of the local molecular field in diamagnetic substances must be located in the individual atoms. The molecular field is then a result of the co-operation of these atomic fields when the molecules become related to one another in a definite way in the crystalline structure. It is pointed out that such fields residing within the atoms are identical with the magnetic atom fields of Ritz and Humphreys, and probably also with the field of the magneton.

In conclusion, a discussion of the nature of the molecular field is given (§ 8). This field must be localised to a large extent in all substances in order to satisfy the condition of continuity of magnetic induction. I hope to publish further extensions of this work in a future communication.

The Transmission of Electric Waves over the Surface of the Earth.

By A. E. H. LOVE, F.R.S.

(Received December 19, 1914.)

(Abstract.)

An analytical solution of the general equations of electrodynamics is obtained for the case of waves generated by a vibrating doublet in presence of a conducting sphere, and is adapted to obtain the known solution for perfect conduction, and the correction for moderate resistance, such as that The known solution is expressed by the sum of a series involving zonal harmonics, and the correction by a similar series. Different results have been obtained by different writers who have investigated the numerical value of the former sum. In the paper a new method of summing the series is explained, and worked out in detail for the wave-length In the case of perfect conduction the result confirms that found The effect of resistance is found to be a slight by H. M. Macdonald. increase of the strength of the signals at considerable distances, counteracting to some small extent the enfeebling effect of the curvature of the surface. A comparison is instituted between the results of the theory and those of recorded experiments. From these it had previously been inferred that the diffraction theory fails to account for the facts; but, after a discussion of the experimental evidence, it appears that the observations may admit of a different interpretation, according to which the results of the diffraction theory would be in good agreement with those of daylight observations at great distances.

* 'Proc. Roy. Soc.,' A, vol. 90, p. 50 (1914).

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On the Origin of the Indo-Gangetic Trough, commonly called the Himalayan Foredeep.

By Colonel Sir Sidney Burrard, K.C.S.I., R.E., F.R.S., Surveyor-General of India.

(Received July 31, 1914.)

1. The Question under Discussion.

The plains of Northern India consist of alluvial deposits brought down by the Rivers Indus and Ganges. These plains conceal from our view a deep trough that has been formed in the solid rock of the Earth's crust. The trough is bounded on the north by mountains of the tertiary age and on the south by an ancient pre-tertiary tableland. North of the trough the Earth's crust has undergone continual compression, disturbance, and uplift since the beginning of the tertiary age; south of the trough it has remained undisturbed since the close of the palæozoic era. On fig. 1 are shown the Indo-Gangetic trough, the mountainous area on its north, and the tableland on its south.

From the writings of Suess, the Indo-Gangetic trough has come to be called the Himalayan foredeep. In this paper I am proposing to consider one question only, namely, the origin of the Himalayan foredeep.

2. The Zone of Low Density in the Crust.

In 1912 I published a paper in which I endeavoured to show that a zone of low density underlies the Indo-Gangetic alluvium and skirts the southern foot of the Himalaya Mountains.†

The existence of this line of low density in the crust has not been disputed. Its significance lies in the fact that it furnishes an argument against Prof. Suess's theory of Himalayan formation. Prof. Suess held that the mountains of Tibet and Persia are advancing southwards in a great series of folds.

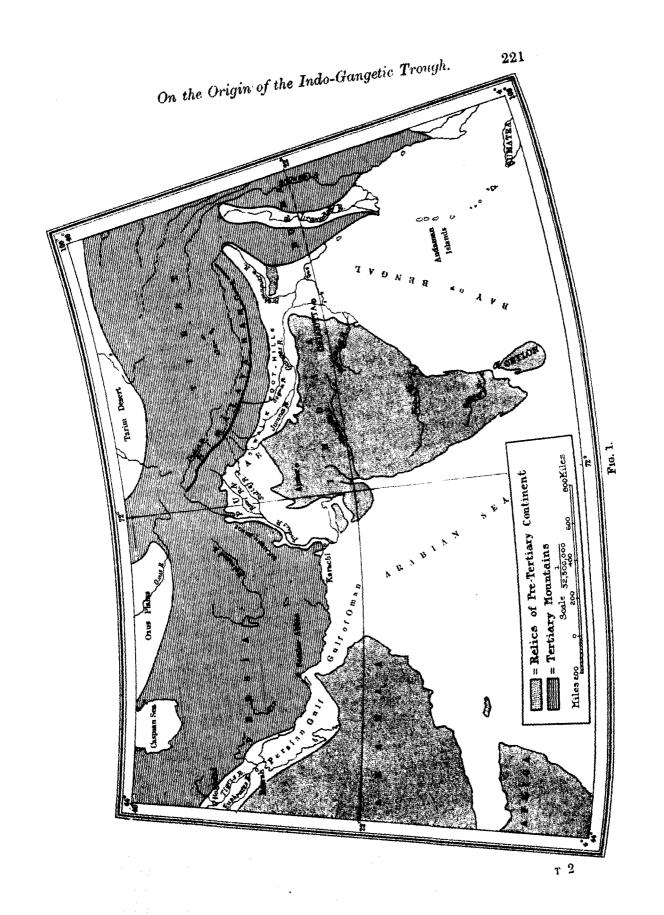
Mr. Hayden, Director of the Geological Survey of India, writes that the great series of folds in Central Asia are supposed to have been caused by a horizontal thrust from the north.§

^{* &#}x27;Geology of India,' p. 2, R. D. Oldham.

[†] Survey of India Professional Paper No. 12, 'On the Origin of the Himalayan Mountains.'

^{1 &#}x27;The Face of the Earth,' vol. 1, p. 596.

^{§ &#}x27;Sketch of Geography and Geology,' p. 48.



Mr. Middlemiss speaks of "the well-established forward march" of the Himalaya range.*

Mr. Oldham states that there has been a southerly advance of the margin of the hills since the Upper Siwalik age. †

It will thus be seen that geological authorities have adopted the theory that the Himalayas are advancing southwards towards the foredeep.

The discovery of a zone of deficient density in the crust skirting the Himalayan foot led me to ask this question: Is the existence of this long line of deficient density lying south of the Himalayas compatible with the view that the crust of Asia is being pushed southwards by a tangential force from the north?

My conclusion was that the existence of this deficiency of matter throughout the northern zone of the Indo-Gangetic alluvium was a strong argument against the theory that the Himalaya Mountains are moving southwards.

The Himalayas are a portion of the plateau of Perso-Tibet, and this plateau appears to me to owe its elevation partly to direct vertical uplift and partly to horizontal thrusts. Horizontal forces from the north and the south seem to have squeezed the plateau between them; on the north side of the plateau the horizontal thrust seems to have emanated from the low-lying plains of the Oxus and from the deserts of Tarim (fig. 1), and to have acted in a southerly direction; on the south side the horizontal thrust seems to have emanated from the low-lying plains of the Euphrates, Indus, and Ganges, and to have acted in a northerly direction.

I closed my paper of 1912 by suggesting that the Himalayan foredeep had been caused by a tension in the crust and that it was, in fact, a crustal opening or rift.

I made use in places of the word "crack." The objection has since been raised that the sub-crust of the Earth is in too viscous a state to "crack." It has been stated that by the use of the word "crack." I have assumed that the sub-crust is solid, and behaves like a solid. I do not, however, wish to make any such assumption, nor do I wish to insist on any particular word. Here, in front of the Himalayas is a deep trough; this trough has been attributed by some authorities to horizontal "compression" of the Earth's crust; it has been attributed by others to "depression" of the crust by the weight of alluvial deposits.

I ask that the hypothesis of an "opening" of the crust may be considered side by side with these hypotheses of "compression" and "depression." If the sub-crust is regarded as solid, the word "crack" will define my meaning;

^{* &#}x27;The Kangra Earthquake,' p. 340.

^{† &#}x27;Geology of India,' p. 470, R. D. Oldham.

if the sub-crust is regarded as viscous, the words "tension" or "stretching" or "opening" can be substituted for the word "crack."

3. The Siwalth Foot-hills.

Wedged in between the Himalaya Mountains and the Indo-Gangetic trough is a narrow zone of low foot-hills called the Siwalik Hills. It is open to question whether these hills ought to be classed with the mountains or with the "foredeep."

The materials composing the Siwalik Hills are so similar to the recent alluvial deposits that they are regarded as an elevated portion of the Indo-Gangetic plains.

Compared with the great ranges of the Himalaya and Tibet, the Siwalik range is insignificant; compared with the alluvial deposits filling the Indo-Gangetic depression, the Siwalik masses are small. In discussions of Himalayan questions, the Siwalik Hills assume importance, because they are always before our eyes. Popular and crowded European stations are situated in the outer hills, and we are apt to attach undue importance to our surroundings.

But in the formation of the Himalaya Mountains on the one side and of the Himalayan foredeep on the other, these small intermediate Siwalik Hills are mere secondary effects.

The strata of which the Siwaliks are composed date back to early tertiary times, and throughout this period have been subjected to horizontal compression and to disturbance. Although they have undergone long-continued tangential compression, these hills have not been elevated into mountains like the neighbouring Himalaya. The explanation of this difference is, I think, that the Himalaya Mountains have been upraised by forces acting at great depths in the Earth's sub-crust, whilst the Siwalik Hills have been formed out of the outer crust. The foundations of the Himalaya Mountains extend downwards to depths perhaps of 50 miles or more; the Siwalik Hills are wholly superficial. I attribute the compression of the Siwalik strata to the opening of the Himalayan foredeep; as the foredeep opens, the superficial strata along its northern edge are squeezed against the Himalayan Mountains.

4. Mr. Oldham's Explanation of the Himalayan Foredeep.

The explanation of the origin of the Himalaya Mountains given in Mr. Oldham's 'Geology of India,' pages 471-474, is based upon the Rev. O. Fisher's theory that the crust of the Earth is floating upon a fluid magma. It would be beyond the scope of this paper to enter into the details of the

Fisher-Oldham theory of mountains, as I wish to confine myself to Mr. Oldham's recent paper in these 'Proceedings,' vol. 90. The main feature of that paper is his discussion of the Indo-Gangetic trough. In his opinion this trough has been created by the sinking of the crust under the weight of the alluvial deposits brought down from the mountains by the rivers.

To quote his own words:—"The load thrown on D (the alluvial plains) will cause it to sink specially in the neighbourhood of A (the Himalayas) where the load is greatest, till the magina displaced by the lower surface of the crust is sufficient to float the load."*

Mr. Oldham's explanation of the Indo-Gangetic trough is that it is a "depression" due to the sinking of strata under their own weight.

Prof. Suess's explanation is that this trough is a downward bend of the crust of the Earth in front of the advancing Himalayan wave. Mr. Oldham attributes the trough to vertical subsidence and "depression"; Prof. Suess attributes the trough to horizontal "compression" from the north.

I have ventured to suggest that the trough has been due neither to "depression" under weight of load, nor to "compression" by horizontal force, but to the opening of the sub-crust under "tension." Three different hypotheses have thus been submitted for consideration. Of these Suess's hypothesis of "compression" has been severely criticised by Prof. James Geikie in Chapter XI of his recent work, 'Mountains—their Origin, Growth, and Decay.'

In this paper I propose to consider the two hypotheses of "depression" and of "tension" and to explain my reasons for thinking that the hypothesis of a sub-crust opening under tension is more in accordance with observed facts than the idea of strata being depressed under their own weight.

Mr. Oldham accepts the existence of the geodetic line of low density, and his explanation of that line, i.e. of the Himalayan foredeep, is this: 15,000 to 30,000 feet of sediment have been deposited by the Himalayan rivers at the foot of the mountains; the Earth's crust has been insufficiently rigid to support these deposits, and the latter have continued to sink deeper and deeper into the solid crust.

With reference to this theory of strata sinking under their own weight I beg to invite the attention of geologists to the following considerations:—

^{* &#}x27;Geology of India,' p. 474, R. D. Oldham.

[†] Mr. Oldham sees evidence of compression in the Siwalik Hills, but he thinks that the compression caused by the advance of the Himalayas "will elevate the marginal" deposits"; he does not attribute the trough-like form of the Himalayan foredeep to "compression."

5. First Consideration: The Weight of the Load.

If alluvium of density 2·1 is resting in rock of density 2·7, as Mr. Oldham assumes, like an iceberg rests upon water, the portion above sea-level will be two-sevenths of that below sea-level; if alluvium has been pressed down by its own weight to a depth of 20,000 feet, displacing a denser substance, we ought to see 5700 feet of it standing above sea-level; if it has been pressed down by superincumbent weight to 30,000 feet, there should be 8600 feet above sea-level. The actual height of Jalpaiguri, Mr. Oldham's station on the alluvium, is, however, only 280 feet above sea-level.

Mr. Oldham's assumed sub-crustal magma is denser than the crust floating upon it. If my calculations are to be made rigorous, we must compare the weight of the alluvium with the weight, not of displaced rock, but of displaced magma; and the alluvium will then be computed to be standing at a greater height even than I have deduced above. The fact that it does not stand at any such height is a strong argument against the hypothesis of a quasiliquid interior for the Earth as well as against the general idea of sinking strata.

6. Second Consideration: The Tuscarora Deep.

The Himalayan foredeep resembles the Japanese foredeep, commonly known as the Tuscarora Deep; these two foredeeps, though differing in certain particulars, have so many features in common that they are believed to have originated from similar causes. The Himalayan foredeep is now filled with alluvium, the Japanese foredeep is still filled with sea-water. The Japanese foredeep will possibly be filled with sedimentary deposits in time, but its existing trough-like form cannot be attributed now to the weight of deposits. The existence of a long trough, between 5 and 6 miles deep, that has obviously not been caused by deposits, is a strong proof that the Himalayan foredeep has also originated independently of the deposits which now fill it.

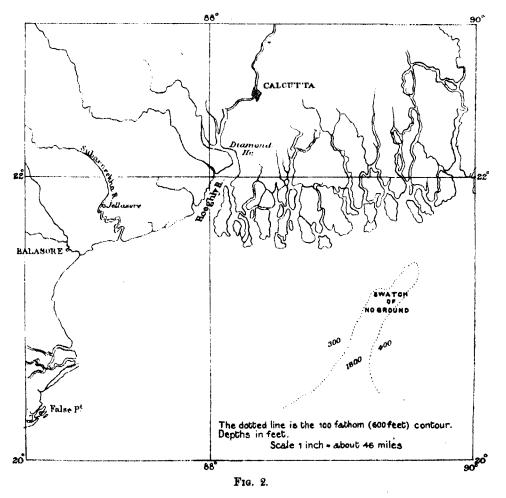
7. Third Consideration: The Submarine Swatches.

To the best of my belief the Indo-Gangetic trough is continued out to sea, both on the east and on the west. I attach two small charts (figs. 2 and 3), which show the submarine troughs extending seawards from the deltas of the Ganges and of the Indus. These troughs have not yet been filled with alluvial deposits, they are antecedent to the deposits. It is a significant fact that in Indian waters the only rivers that are continued seawards by submarine troughs are the Ganges and the Indus. The Godaveri, the Caveri, the Kistna, have no such troughs extending beyond

^{* &#}x27;Geological Magazine,' vol. 10, No. 591, p. 387, September, 1913.

their deltas. The submarine troughs of the Ganges and Indus will doubtless be filled with deposits in time, and our successors may then be led to believe that the troughs were created by the weight of these deposits.

In early tertiary times, before the existing loads of silt had been brought



down from the mountains by the rivers, the Indo-Gangetic trough had already been formed and was a narrow arm of the sea.*

8. Fourth Consideration: How Rivers Deposit their Loads.

Mr. Oldham writes that the load of silt thrown on to the plains will cause them to sink, "especially in the neighbourhood of the Himalayas where the

* H. H. Hayden, 'Sketch of Geography and Geology of the Himaleyss,' p. 255. See so charts in McCabe's 'Story of Evolution.'

load is greatest." He assumes, therefore, that a river debouching from the Himalayas will deposit the greatest portion of its load near the point where it leaves the hills, and that as the load of silt sinks into the crust the amount of crustal subsidence along the course of the river will be greatest where the river leaves the hills.

Let us take two contiguous Himalayan rivers, the Ganges and the Jumna; the Ganges leaves the mountains at Rikkikesh, the Jumna leaves them at

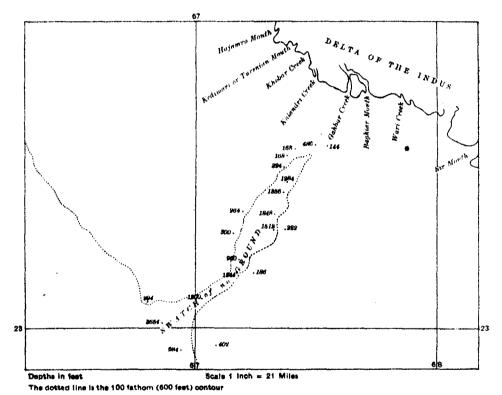


Fig. 3.

Kalsi. Rikkikesh is 45 miles from Kalsi. The great load of silt brought down by the Ganges will (according to the theory of "depression by weight") cause a sinking of the crust near Rikkikesh, whilst the load brought down by the Jumna will cause a subsidence near Kalsi. But why should these silt-loads of the Ganges and Jumna cause subsidence of the crust throughout the 45 miles that intervene between Rikkikesh and Kalsi? The geodetic observations have led us to believe that there is a deep invisible trough skirting the foot of the mountains; we have no geodetic data in support of the view that the depth of this trough increases at

points where rivers emerge from the hills and decreases at intermediate points. The geological theory demands not a continuous trough in the crust, but a series of basins under Hurdwar, Kalsi, and similar riverain points.*

9. Fifth Consideration: The Hidden Troughs of the Punjab.

Mr. Oldham, dealing only with the eastern half of the Indo-Gangetic trough (see fig. 1), shows in his diagram that the alluvial deposits of a river are a maximum at the foot of the mountains and decrease gradually as the river recedes from the mountains. On its northern margin, he writes, the depth of the alluvium is great, on its southern margin its thickness is small; the depth, he assumes, "decreases gradually from north to south." But let us apply this hypothesis to North-Western India, to the plains of the Indus and Sutlej (see fig. 1). The Punjab is bounded on the north-west by the Sulaiman range and on the north-east by the Himalayas (fig. 1). We have reason to believe, though the evidence is not yet complete, that a trough filled with alluvium skirts the feet of both ranges; this deficiency of matter runs round the edge of the Punjab plains: in the centre of the Punjab is an excess of matter. The alluvial deposits over the Punjab have, however, been brought down from the Himalayas by the Indus, Jhelum, Chenab, Ravee, Beas, and Sutlej (fig. 1). Where the Ravee leaves the Himalayas, near l'athankot, a deep hidden trough exists; this trough should, according to the "depression by weight" theory, become shallower as the Ravee crosses the Punjab; it does become shallower for a certain distance, but on the west of the Punjab becomes deeper again, namely, along the foot of the Sulaiman Mountains; † this deepening demands, according to Mr. Oldham's theory, a new source of alluvial deposit, and as we found the source of the eastern deposits in the Himalayas so we naturally turn to the Sulaiman Range to supply the western ones; but the rivers of the Sulaiman have always been insignificant, compared with those of the Himalaya, and their alluvial deposits have been trifling compared with those of the Indus; and we find that whereas the association of a trough of deficient density with the foot of a mountain range holds good on both sides of the Punjab, the association of this trough with sources of alluvial deposit holds good only on one side; if, therefore, the weight of the alluvium was not the cause of the trough below the Sulaiman Mountains, it is difficult to argue that it must have been the cause of the trough below the Himalaya.

^{*} This theory will be tested geodetically.

[†] See Plate 5 of Lenox-Conyngham's 'Pendulum Operations in India.'

10. Sixth Consideration: The Bore-Holes,

The plains of Northern India are deposits of silt brought down by rivers from the Himalayas. Bore-holes have been sunk and remains of organic life found buried at great depths in the silt; it has been assumed that the rockfloors underlying the Indus-Gauges valleys have been continually sinking under the increasing weight of the deposits. Both on the west and on the east, long, deep, narrow, submarine troughs extend out into the oceans in continuation of the Indus and Ganges valleys. The waters of the Indus and Ganges are continually pouring silt into these troughs; amongst the silt are remains of organic life that once flourished at sea-level—plants, shells, bones and these are being deposited at great depths in the troughs. The assumption that organic remains found at depths in bore-holes must have been originally deposited at sea-level is thus not justified. The simplest explanation is that the plains of Northern India are concealing a sub-crustal crack, that the submarine troughs are continuations of the crack, and that as the crack has opened and grown deeper, the deposits filling it up have been continually sinking to lower levels.

11. The Subterranean Form of the Indo-Gangetic Trough, the Slope of its Rock-walls, the Depth of its Rock-floor.

In my original paper on this subject I emphasised the fact that a band of low density exists in the crust along the northern border of the Indo-Gangetic trough. I thought that this band of low density indicated an opening in the Earth's crust, and this view was strengthened by the topographical appearance of the Indo-Gangetic trough, the parallel sides of which give the idea of a crack in our planet (see fig. 1). But I did not presume to deduce any value for the depth of the trough from the geodetic results.

It is true that I did refer on one occasion to a possible depth of 20 miles, but this figure was independent of the geodetic results: I suggested 20 miles for the depth of the crack, because that is the depth at which earthquakes have their origin in our time.

The geodetic results justify the conclusion that a line of low density exists; Mr. Hayford writes to me from America:—

"Your present work is certainly very effective in showing clearly the existence of a belt of defective density and a belt of excessive density each crossing India. No future investigation will contradict those two conclusions."

The line of low density is proved, but we cannot determine the exact form of the trough. I admire the skill with which Mr. Oldham has grappled with

the geodetic problem, but still the figures in his paper, published by the Royal Society, have all been based on three uncertain assumptions:—

Firstly, he has had to assume that the Himalaya Mountains are everywhere in complete local isostatic equilibrium; secondly, he has had to assume certain values for the densities of alluvium and rocks at great depths; and, thirdly, he has had to assume an intimate knowledge of deep-seated geological formations in a foredeep, the origin of which is unknown.

There is evidence to show that the Himalayan mass is largely compensated, as a whole, but when we come to numerical calculations it is unsafe to assume that the compensation is locally effective.*

Mr. Oldham has told us that 15,000 to 30,000 feet of sediment have been deposited along the foot of the Himalayas, and that these deposits have sunk into the Earth's crust, and created a trough by their weight. These deposits, lying in their self-made trough, he calls the "invisible topography," and he tells geodesists that they must make allowance in their calculations for the invisible as well as for the visible topography. But what happens when these deposits are disturbed? Geologists have found that these deep deposits have in places been elevated above sea-level.

Mr. Oldham himself writes in the 'Geology of India,' p. 470: "The Siwaliks now form low hills, in which these once horizontal deposits have been disturbed, elevated, and exposed to denudation."

Where, then, is his invisible topography? Is it lying in its bed undisturbed, or has it been uplifted? If it has been uplifted, has the old rock which the alluvium depressed been uplifted also. In his calculations Mr. Oldham has assumed the existence of undisturbed deposits, when the latter are known to have been elevated. On p. 40, 'Proceedings of the Royal Society,' vol. 90, Mr. Oldham draws the deepest part of his undisturbed trough exactly under the zone where the deposits have been elevated.

If we observe the plumb-line or pendulum at the Earth's surface, we constantly obtain results that have no apparent topographical or geological explanation; we find the plumb-line deflected away from visible mountains, we find it deflected towards oceanic hollows, we even obtain abnormal results when observing upon desert plains. It is evident that there exist invisible deep-seated causes. The calculation of the depth at which these invisible causes are situated is a complicated problem. If we make different assump-

^{*} A large floating iceberg is in equilibrium as a whole; its visible masses above sealevel are compensated by invisible masses below sea-level as a whole. But every ice pinnacle of the berg is not individually and locally compensated by a corresponding root of ice. Under the Himalayan station, Mussooree, height 6924 feet, the compensation appears to amount only to three-fourths of the visible mountain.

tions concerning the dimensions and densities of a hidden disturbing cause, any number of different values of the depth can be found to satisfy the geodetic results.

Mr. Oldham has taken the plumb-line observations of a few stations and has endeavoured to show that these observations can be explained on the hypothesis that the Gangetic trough is $3\frac{1}{2}$ miles deep.

It is easy, however, by slight changes in the assumptions to obtain greater values for the depth of the foredeep than 3½ miles, and I do not know why the smaller value should be preferred to the greater.

Mr. Oldham, wishing then to show that a rift would not produce effects in accordance with geodetic results, assumes a rift of symmetrical section, 17 miles deep, 5 miles wide.* I agree that this assumed rift does not accord in any way with the geodetic results. The only references that I made in my memoir to the form of the Indo-Gangetic rift were as follows:—

- (i) "The Himalayan side of the rift appears to be a steep wall, the southern side has a gentle slope" (p. 3).
- (ii) "There has been a succession of cracks in successive sub-crustal shells. On each occasion that the rift has become deeper, it has opened further north than before. Only by such an hypothesis am I able to explain the steepness of the wall on the north side of the rift and the gentleness of the slope on the south side "(p. 7).

The above extracts will show that the idea of a symmetrical rift, 17 miles by 5 miles, has not been derived from my paper.

The Himalayan foredeep has, I think, the same form as the great deeps off the coast of Asia; the following extracts are borrowed from Prof. James Geikie's recent work on 'Mountains: their Origin, Growth, and Decay':—

"On the accompanying map, a section across the Pacific from Japan to North America shows the Tuscarora deep of the great Japanese trough. It will be observed that the sea-floor descends from the coast at a somewhat high angle to the depth of 4600 fathoms, after which it rises with a much gentler gradient, until the level floor of the ocean is reached at a depth of a little over 2000 fathoms. The deepest part of the trough, therefore, lies relatively close in shore or at the foot of the continental escarpment.

"The bottom of the Aleutian trough is somewhat irregular, varying in depth from 3000 to 4000 fathoms. It extends from the Alaskan Peninsula along the whole front of the arc of islands, and is almost continuous with the enormous Japanese depression. The latter skirts the outer coasts of the Kurile Islands, Japan, and the Boniu Islands, with a depth ranging between

^{*} Such dimensions as 17 miles by 5 miles were not mentioned in my paper.

3000 and 4000 fathoms, the deepest part of the trough throughout its whole extent lying nearest the land.

"The Philippine trough begins opposite the Riu Kiu Islands, and extends along the whole eastern margin of the Philippines to Tulur Island, at a depth of 3000 to 4700 fathoms, the greatest depths, as in all other cases, lying closest in shore."

Geodetic observations have led us to infer that the rock-floor of the Himalayan foredeep has a steep slope on the side of the mountains and a gentle slope on the opposite side. It would, however, be unsafe to assume that these surface forms are the results of superficial causes. The compensation of mountains and continents extends, according to Mr. Hayford, to a depth of 70 miles; the Himalayan and Japanese foredeeps are both lines of constant seismic activity, and the earthquakes are believed to occur at depths exceeding 20 miles. The forms of the Himalayan and Japanese foredeeps are possibly the effects at the Earth's surface of deep-seated sub-crustal movements.*

The idea I have formed of the Indo-Gangetic trough and of the Tuscarora deep is that sub-crustal shells have been cracking under tension, and that the cracks have been followed by sub-crustal movements (due to shrinkage at considerable depths) towards the side of the mountains. The cracks may have become filled, partly by lava flows from below, partly by slow rockflows from the sides, and partly by débris from above. All that we know of the materials filling the trough is that they are abnormally light.

Before I leave the question of the form of the trough, I must refer for one moment to the position of that point at which the depth is a maximum. Mr. Oldham makes this point actually under the Siwalik Hills (see his diagram on p. 233). The geodetic observations lead me to place the greatest depth of the trough altogether south of the Siwalik Hills, and many miles south of Mr. Oldham's position.

In the 'Geological Magazine,' vol. 10, No. 594, pp. 532-536 (December, 1913), Mr. Oldham wrote as follows:—

"Every observer, in every part of the range which has been visited, has found evidence of compression in precisely that zone where Colonel Burrard's postulate demands extension."

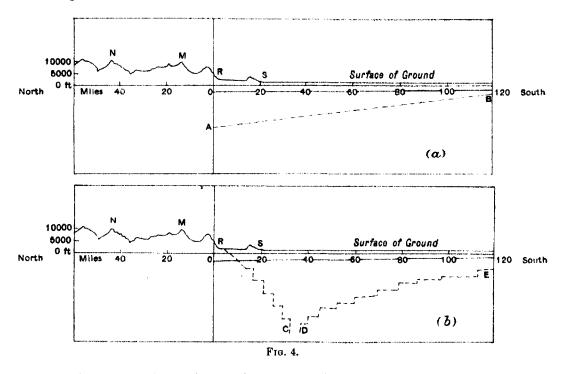
Geologists have, it is true, found evidence of compression in the mountains,

* The width of the Himalayan foredeep varies from 350 miles in North-West India to 100 miles south of Nepal. Captain Couchman, in charge of the pendulum observations, is of opinion that the deepest part of the Himalayan foredeep is not where the alluvial deposits stand highest above sea-level, but is opposite to Eastern Nepal, where the Himalayan range is at its highest.

but not in the "foredeep"; my postulate demands extension in the foredeep only, not in the mountains. I submit that the yielding to tension under the foredeep has been the cause of the compression in the mountains.

Whilst I have no means of determining either the depth of the Himalayan foredeep, or the densities of the rocks and débris that are filling it, I give in fig. 4 (b) a rough diagram to illustrate my idea of the form of the trough.

The figure 4 (a) is copied from Mr. Oldham's paper, p. 40, 'Proceedings of the Royal Society,' vol. 90 (1914). M and N represent the Himalayas, R to S represents the Siwalik foot-hills. This figure 4 (a) illustrates Mr. Oldham's



explanation of the foredeep. The bottom of his foredeep is shown by means of the dotted line AB. His idea of the form of the foredeep is RAB. According to his explanation river deposits have sunk by their weight to the depth of the line AB, and RAB is the "invisible topography." He believes that the Himalayas, NM, have moved southwards and have crumpled up the Siwalik foot-hills at R and S. He places the deepest point of the foredeep at A, i.e. at the northern edge of the Siwalik foot-hills.

Fig. 4 (b) illustrates my idea of the form of the foredeep, which I have drawn with a dotted line. I place the deepest point of the foredeep at D, i.e. south of the Siwalik foot-hills. The depth of D is unknown.

The explanation which I beg to offer is that the Earth's figure and onter shells have been under tensile strain and that the foredeep has opened from E to C. As the sub-crust at C has been forced to move northwards, the Himalayas at M and N have been uplifted vertically, and the Siwalik deposits at S and R, after sinking into the rift, have been uplifted and pressed against the Himalayas.

12. The Hypothesis of a Rift.

I am indebted to Mr. J. de Graaff Hunter, M.A., Mathematical Adviser to the Survey of India, for the following note upon the cooling of the Earth and upon cracks in the sub-crust.

Note on Cooling of the Earth and Cracks in Sub-crust.

By J. DE GRAAFF HUNTER, M.A.

It appears to me that the early state of the Earth must have been such as described by Lord Kelvin.*

The state presupposed is a globe in a fluid state, on account of its high temperature, losing heat by radiation; this is the first stage. I think it is unnecessary to go further back and discuss the most probable way in which this state was arrived at; it appears a highly probable early state. The subsequent history of such a globe would be as follows:—First of all an outer layer would cool and eventually solidify. If, as occurs in practically all known substances—and surely in the great bulk of the materials which make up the Earth—the material of the crust contracts with cooling, it accordingly becomes more dense than the fluid below it, and it breaks up and sinks into that fluid. Probably it melts again, but by doing so it chills the surrounding fluid to some extent. This process seems to be continuous until a solid core is formed; and this core will keep or increasing in size as the successive surface crusts fall in, until we eventually arrive at the second stage—a solid globe of nearly uniform temperature. The uniformity in temperature is due to the convection effect of the successive sinking of the crust and rising of molten matter from below.

When the whole globe is solidified, this convection ceases and the result is a very rapid cooling of the outer crust, which now depends for its heat on conduction from the interior of the globe. After a comparatively short time the crust approximately reaches its final temperature, which depends on the exchange of radiation between the Earth and other bodies of the universe. This is the third stage. Considerations of radioactive substances may slightly modify this result, but not in a way which affects the subsequent argument. During this process of cooling of the crust, cooling below has also been going on, but at a much smaller rate. The contraction, which has already been assumed to accompany cooling, must during the third stage have thrown the crust into a state of great tension. We have to consider the crust cooling rapidly from a temperature of the order of that of melted rock to a temperature such as prevails at present at the Earth's surface. Inevitably cracks must occur. This state of affairs is prior to the existence of oceans, for the temperature until nearly the end of this state would be above the boiling-point of water. There would not be any rush of water into such cracks, but gravity

^{* &#}x27;Mathematical and Physical Papers,' vol. 3, Art. XCIV.

would be sufficient to partially close them up by the upper edges of the crack breaking off, until the slopes attained the angle at which equilibrium was possible. Later on, the water would condense and find its level round the globe. By so doing it seems probable that the level (equipotential) surfaces throughout the globe would be disturbed and further fractures might take place, probably with a tendency to follow parallels of latitude.

By this time the fourth stage has begun, in which the surface of the Earth would be, as regards temperature and existence of oceans, similar to what it is now. It would not be an exact geometric figure, but I imagine the main features would be continents and oceans and the cracks which occurred in the third stage, and that there would not be any appreciable mountains. The increase of temperature with depth near the crust would at the beginning of the fourth stage be very much more rapid than it is now, and the material a little way in from the surface would continue to cool at a rate which was now greater than the rate at which the crust would be cooling, the crust having now approximately reached a steady temperature. The inner earth would then proceed to contract more rapidly than the crust. It would itself crack, and the most likely places for such cracks to occur would be those already exposed to air or ocean by the cracks of the outer crust. In such cases the débris which had fallen into the outer cracks would sink lower into the earth. This cooling of the portion below the outer crust would result in one of two things, or a combination of them, namely (1) the crumpling of the crust and (2) the slipping of the crust and attendant partial closing up of its cracks. These surface cracks, however, could never be wholly closed up by contraction of interior matter until the whole Earth had reached a steady (low) temperature.

As time went on, lower and lower levels would reach the state of contracting more rapidly than those both below and above them, resulting in cracks in the particular layer and a tendency to crumpling, or closing up of cracks, in the upper layers. We are apparently now at the stage when this effect has penetrated to the comparatively small depth at which earthquakes have their origin. It appears that, as this depth increases, the chances of crumpling of the upper layers diminish and that of the partial closing of cracks increases. But, as I have said above, the cracks cannot be entirely closed up by contraction alone until the whole Earth is cooled.

A further effect is to be expected. The cracks which are formed in any layer, except a few of the uppermost, will in due course be partially filled up by fractured material falling down from an upper layer; and with contraction in still lower layers (due to further cooling) will be entirely closed. Still further contraction below will inevitably cause crumpling, for there is now no alternative in the way of cracks closing. This crumpling in the lower layers must cause a vertical lifting of the surface layers, which will then form mountains. The cracks in the surface layer will not, in the main, be closed by this upheaval, for the area of the lower layers has been increased by crumpling, and the surface layer must either stretch or crack to accommodate itself to the enlarged area on which it rests. In this way new cracks might actually open, while mountains were being formed in the outer crust.

It appears impossible to assign any limits to the depths up to which this effect might occur.

The cracks on the outer surface could never be wholly filled up. They would only be partially filled by fractures in the third stage and by the products of denudation in the fourth stage.

The following is an extract from Prof. Shaler's 'Comparison of the Features of the Earth and Moon,' p. 8:—

"The surface of the moon exhibits a very great number of fissures or rents, VOL. XCL.—A.

which when widely open are termed valleys, and when narrow, rills. Both these names were given because these grooves were supposed to have been the result of erosion due to flowing water. The valleys are frequently broad; in the case of that known as the Alpine valley, at certain places several miles in width; they are steep-walled, and sometimes a mile or more in depth; their bottoms, when distinctly visible, are seen to be beset with crater-like pits, and show in no instance a trace of water-work, which necessarily excavates smooth descending floors such as we find in terrestrial valleys. The rills are narrow crevices, often so narrow that their bottoms cannot be seen; they frequently branch, and in some instances are continued as branching cracks for 100 miles or more. The characteristic rills are far more abundant than the valleys, there being many scores already described; the slighter are evidently the more numerous; a catalogue of those visible in the best telescopes would probably amount to several thousand.

"It is a noteworthy fact that in the case of the rills, and in great measure also in the valleys, the two sides of the fissure correspond, so that if brought together the rent would be closed. This indicates that they are essentially cracks which have opened by their walls drawing apart."

The "canals" of the planet Mars have given rise to much interesting discussion. I have no right to express an opinion upon this subject, but as astronomers have differed widely in their views, I may perhaps be permitted to invite the attention of students of Mars to the rifts on the Moon's surface and to the apparent rifts on the Earth's surface, and to ask whether the canals of Mars may not be openings in its outer crust.

Mr. Hunter, in his note which I have quoted above, has considered a cooling globe, and has shown that it is liable to crack. This liability will be increased by the strains to which the Earth's figure and upper crust are subjected. If the Earth's rotation has decreased in the past, the spheroidicity of its figure must have decreased also. The superfluity of rock accumulated at the equator under a higher rotation velocity could not have moved to the poles without great distortions of the rock surface occurring.

It has been estimated that the Earth picks up from 10 to 20 millions of tons of additional matter from space in the shape of meteors every year. If at any time in the past the Earth was ever struck by a very large body from space, ages may have ensued before the Earth's figure was able to accommodate itself to the new conditions. In geological history there appear to be epochs, especially the Permian and the Cretaceous, when large changes of figure began, and it may have been that some abnormally large addition of rock was then picked up by the Earth from space.

Even the accumulation of ice at the poles in the glacial epoch may have

been sufficient to affect the spheroidicity of the Earth, and to set up strains in its outer shells.

13. Departures from Isostasy.

It has been shown by geodetic observations that the Earth's crust is in a condition approaching isostatic equilibrium. If any departure from isostasy occurs, the Earth's figure becomes subjected to strains, and its surface becomes liable to crack (or to stretch). A considerable departure from isostasy cannot persist indefinitely; the force of gravitation and the Earth's retation are always tending to produce complete isostasy. When isostasy is disturbed by the irregular cooling of the sub-crust, or by the slowing down of the Earth's rotation, or by the impact of meteors, or by the conversion of equatorial water into polar ice, equilibrium can be restored by the compression of the crust in some regions and by stretching of the crust in others. Crustal tension and crustal compression are among the means by which isostasy is maintained.

The readjustments in the isostasy of a continent that become necessary, as the Earth undergoes changes, may bring about disturbances in the isostasy of smaller regions.

In India, the Indus-Ganges trough appears to have been opening northwards, and the Himalaya Mountains seem at the same time to have been undergoing elevation along the northern edge of the trough. If this view is correct, a certain amount of rock must have been moved northwards out of the trough into the mountains. The northward movement may have been caused by the cooling of the Earth or by readjustments of its figure or mass to new conditions. The disturbing effects upon local isostasy of this northward movement have been partially counteracted by denudation, for, although rock-mass may have been moved northwards by the opening of the trough, rivers have been bringing silt southwards from the rising mountains and pouring it back into the trough.

In this paper I have discussed the hypothesis that the Earth's crust is being depressed by the weight of riverain silt deposited upon it, and it may not be out of place to attempt to discover from observation the weight of actual loads which the Earth's crust is seen to be supporting.

Colonel Lenox-Conyngham writes: "Under the Himalayan station of Mussooree, height 6924 feet, there appears to be standing above sea-level an extra uncompensated mass equal in bulk to about a quarter of the visible mountain."

This is Colonel Conyngham's deduction of the most probable result; he emphasises the fact that there are elements of uncertainty in the calculation.

A considerable departure from isostasy is exhibited by the Ranchi Plateau. This plateau forms part of the Vindhya Mountains, and is a relic of an ancient tableland; it is situated immediately south of the Indus-Ganges trough in longitude 84°, opposite to the Himalayan peaks of Mount Everest and Dhaulagiri. Ranchi lies near the crest of the "hidden chain" of excessive density. The pendulum observations seem to indicate that the Ranchi Plateau is mainly supported by the rigidity of the Earth's crust; and the plumb-line observations show that there is a considerable excess of mass south of the Ganges at Ranchi. The Earth appears to be supporting this load without appreciable deformation.

As, however, certain geodesists have modified to a slight extent Prof. Helmert's formula for the normal value of gravity, and as the calculation of any departure from isostasy is dependent upon that formula, I asked Colonel Lenox-Conyngham to give me his opinion concerning the load supported at Ranchi. He considers that the Ranchi mass may possibly not be wholly supported by the crust's rigidity, but that probably half of it is. If this cautious estimate is accepted, then the Earth is strong enough to sustain a weight of 1000 feet of rock (density, 2.67) over an area of two square degrees (8500 square miles) without yielding.

I have now given my reasons for thinking that the hypothesis of a subcrust opening under tension is more in accordance with observed facts and is more deserving of consideration than the idea of strata sinking under their own weight.

On Thermophones. By P. DE LANGE.

(Communicated by Lord Rayleigh, O.M., F.R.S. Received December 3, 1914.)

The invention which I desire to communicate to the Royal Society (and of which I have already, with the permission of your President, demonstrated the models at your informal gathering on the evening of October 29) has been made by me in co-operation with my friend Otto Fischer. Some of the models have been made in the laboratory of the University of Utrecht by the assistant, Mr. Stellema, under the supervision of my cousin, Prof. Zwaardemaker, who was so kind as to introduce me to Lord Rayleigh. I have been demonstrating with these models for over six months, and they do not show the slightest wear.

The origin of the thermophones may be traced back to the invention made 34 years ago by your late Fellow, the former engineer-in-chief to the Post Office, Sir William Preece.*

Sir William Preece attached a stretched wire to a diaphragm which, by extending and contracting, owing to the changes in an electric current passing through it, moved the diaphragm, and thereby made it speak. The great difference between his invention and that of the thermophone lies in the mechanical action of the wire on the diaphragm, the latter being dispensed with in the thermophone, the action of which simply and solely rests upon a change of temperature in a wire unconnected with any mechanical contrivance. In the thermophone the wire speaks without a diaphragm, and the basis of this invention has been laid by Mr. Gwozdz.

About seven years ago, the Russian engineer, Gwozdz, made various experiments in a small village in the neighbourhood of Lodz, in Poland, with a thermophone without a diaphragm and without an electromagnet. Gwozdz fixed a Wollaston wire on an insulating medium, and then treated the Wollaston wire with acid. He obtained thereby a good thermophone, but (as far as I know) it was impossible by this process to obtain instruments which conveyed the required volume of sound, and Gwozdz never succeeded in rendering the thermophone of any practical utility.

Curiously enough, at the same time, Prof. Abraham, of Paris, made some experiments with a thin platinum wire which he connected with electrodes in a straight line, and then again with a transmitter. These experiments also did not meet with a practical result, because the stretched wire had no

^{* &#}x27;Roy. Soc. Proc.,' vol. 30, p. 408.

freedom, and thereby was exposed to too great a danger of breaking by the alternate extensions and retractions.

With my invention I follow the process of Gwozdz regarding the treatment of the Wollaston wire, but I claim that my invention is of the greatest practical value, and this I will now explain.

By fixing a platinum wire of a diameter of from 2 to 12 microns in a gothic curve, I claim to have succeeded in making the thermophone of practical everyday use, because the silver of the Wollaston wire is eliminated, whilst the whole Wollaston wire is freely suspended in the acid in such a way that at any time such part of the platinum wire can be set free, as is considered desirable, without it being liable to breakage.

Thermophones have value only if they have been made on this basis.

In order to know something more about the working of the thermophone, Prof. Zwaardemaker and myself have measured the volume of the sound with Lord Rayleigh's well-known mirror. In order to avoid currents of air which might originate through the heating of the wire, we placed a glass diaphragm in a wooden or aluminium frame between the wire and the mirror. The size of the diaphragm was about the same as that of a diaphragm of the phonograph. Moreover, we placed a small tube in the cover of the diaphragm in order to prevent the system from working as an air thermometer.

The result of our measurement was that the sound increased with the increased number of platinum wires, but not in the same ratio. Also thin wires of 2 microns have a greater acoustic effect than wires of 5 microns, the Joule heat remaining the same. Everything depends upon the exact relationship between the telephone and the microphone.

The thermophone, listened to in the open air, sounds extremely weak. As soon, however, as the platinum wire is placed under a cover which has a small opening or several small openings, the sound at once becomes clear and distinct. The volume of the sound increases in accordance with the decrease of the size of the cover. Evidently the cover functions as a resonator. It is a telephonic advantage to make the cover as small as possible, because in that case the high notes and the sound consonants produce a better effect. The size*of the openings in small covers should not be made too large, because in that case the resonance becomes too high and produces a curious sound in addition to the human voice. I am trying to find an explanation for this most curious phenomenon, but that is a matter which may be the subject of a future communication to this Society.

The maximum admissible size of the cover appears to vary between comparatively speaking wide limits. The size which approximately agrees with the size of the human ear funnel seems to be the most suitable. Metal covers are better than those of ebonite, and, by surrounding these with some cooling substance, the acoustic effect—if measured with Lord Rayleigh's mirror—becomes twice as great. In this case the sound is conducted through a rubber tube of small width.

It is quite possible to combine a number of these thermophones, but then it should not be forgotten that the whole space occupied by them should remain as small as possible, because the space which they take up together also acts as a resonator.

The acoustic effect appears to increase at least in about the square of the strength of the current.

Thermophones with four rows next to each other, each of six platinum wires of 7 microns with a combined resistance of 35 ohms give—measured with Lord Rayleigh's mirror—the following results, viz.:—

In the case of 6 volts, $2\frac{1}{2}$ degrees.

It is difficult from these items to construct the theory of the thermophone. The most I can say is that the decrease and increase of heat in the platinum wire of the telephone takes place isochronically with the vibrations in the microphone. The air surrounding the platinum wire is thereby immediately heated or cooled in accordance with the increase and decrease of heat in the wire, and, if that air is retained within a closed compass of the cover, the expansions and retractions will be noticed as sound.

The Simplification of the Arithmetical Processes of Involution and Evolution.

By E. CHAPPELL, City and Guilds (Engineering) College.

(Communicated by Prof. W. E. Dalby, F.R.S. Received January 25, 1915.)

It is a self-evident statement that addition and subtraction are the most simple arithmetical processes, so that any other process may be said to be completely simplified when it is replaced by either of these two. The invention of logarithms completely simplified multiplication and division, but only reduced involution and evolution to multiplication and division. In modern applied science there are many laws and empirical formulæ in which fractional indices occur, and the calculations sometimes become troublesome on this account. Although the obvious course is to perform the necessary multiplication or division of the logarithms, in such cases, by the addition or subtraction of their logarithms, no one seems to have considered it worth while to construct a Table giving the logarithms of the logarithms of numbers directly. The only step in this direction is the invention of the "log-log" slide-rule, which is very limited in its range, and the accuracy of its results may be open to question. The prospect of abolishing even multiplication and division from all ordinary calculations, and so making addition and subtraction the only necessary arithmetical processes, was sufficient inducement to the author to construct such a Table.

Before describing the difficulties that had to be overcome, a few words on the proposed nomenclature are necessary. In the first place, the word "logarithm" is unpronounceable and too long, which most people realise and avoid by calling it "log"; secondly, the inverse function has been very clumsily termed "anti-logarithm"; and, thirdly, the logarithm of the logarithm has been given the cacophonous name "log-log." It, therefore, seems permissible to devise more convenient names, constructed on some system. It is proposed to replace logarithm by "log," and to call the inverse function the "illog." The name "log-log" would sound better if reduced to "lolog," and its inverse function could then be systematically named the "illolog."

There are three difficulties encountered in constructing a lolog table:—

- (1) The lolog of unity is infinite, and the differences in that region are very large.
- (2) A base cannot be chosen so that all numbers having the same sequence of digits have the same mantisse.

(3) The logs of numbers less than unity are negative, so that the lologs of such numbers are the logs of negative numbers.

The first of these difficulties is surmounted by diminishing the intervals at which the values are given in the neighbourhood of unity, and the second by limiting the range of the Tables. The third difficulty is avoided by neglecting the negative sign, which is, after all, an external feature that does not affect the numerical result of multiplication or division. For example, $\pm 2 \times \pm 3 = \pm 6$. Whatever the signs of these two factors, the numerical part of the result could be obtained by adding log 2 to log 3. The sign, however, would have to be determined independently.

If the lolog of 0.25 is required, one proceeds as follows:—

$$\log 0.25 = 1.39794 = -0.60206.$$

Therefore

$$lolog 0.25 = log 0.60206 = \tilde{1}.77964$$
;

but it also happens that

$$lolog 4.0 = log 0.60206 = 1.77964.$$

If the number 177964 were given, the difficulty is to know whether its illolog is 40 or 0.25. The neglect of the sign of the log does not mean that merely the sign of the result has to be settled, but the numerical part is affected also. Although a little thought would always decide which is the correct value, the need for such thought would lead to errors and uncertainty, which would make the tables unsuitable for general use. All uncertainty of this nature can be overcome by printing the lologs of numbers less than unity on red paper, and of numbers greater than unity on white paper. The illologs would similarly be printed on red and white paper.

It is clear from the example above that the two numbers which have numerically equal lologs are reciprocals. This property enables reciprocals to be found very readily from lolog and illolog tables.

Let us now consider a simple case of involution and evolution. If it is given that $A^{\mu} = C$, then $A = {\frac{\mu}{C}}$.

Taking logs twice,
$$lolog C = log B + lolog A$$
,
or, $lolog A = lolog C - log B$.

From these two equations two simple rules can be derived:—

- (1) To raise a number to the *n*th power, add the log of *n* to the lolog of the number, and the illolog of this sum is the desired result. The illolog must be found on a page of the same colour as that on which the lolog was found.
- (2) To extract the nth root of a number, subtract the log of n from the lolog of the number, and the illolog of this difference is the desired result.

The illolog must be found on a page of the same colour as that on which the lolog was found.

To obviate mistakes almost entirely, it is recommended that lologs taken from red pages should be written down in red ink, also the result after adding or subtracting a log to or from a red lolog.

It has already been shown that the lologs of reciprocals are equal in magnitude, though different in colour. For this reason, expressions of the form

$$x^{-a} = \frac{1}{x^a} = \left(\frac{1}{x}\right)^a$$

can be evaluated with no more labour than that necessary to evaluate x^a . The rule is:—

(3) When performing a process of involution or evolution on the reciprocal of a number, merely change the colour of the lolog of the number itself, and proceed exactly as stated in Rules 1 and 2.

In the space available, it has not been possible to consider other properties of lologs which, though interesting, have little practical importance.

Involution and evolution of numbers and their reciprocals are of such frequent occurrence that the author ventures to hope the tables in question will prove useful in many different classes of calculation.

A Bolometric Method of Determining the Efficiencies of Radiating Bodies.

By WILLIAM A. BONE, F.R.S., H. L. CALLENDAR, F.R.S., and H. JAMES YATES.

(Received February 15, 1915.)

Introduction.

With the increasing use, within recent years, of gas fires, electric radiators, incandescent surface combustion diaphragms, and the like, there has arisen a demand for a reliable general method for testing their radiant efficiencies. The problem is important also in its purely scientific aspects, inasmuch as its solution would enable the relations between the modes of combustion of various combustible gases and their radiant values when burnt at an incandescent surface to be investigated.

The present paper describes a bolometric method which we believe to be applicable to the measurement of the radiant energy emitted from hot terrestrial surfaces generally, but as the source of radiation in our experiments has been a gas fire, it will be convenient if we describe it with reference to that particular mode of heating.

A typical modern gas fire consists of a series of atmospheric burner nozzles, varying usually between seven and fifteen in number, according to the size of the apartment to be heated, arranged equidistantly along a common horizontal supply pipe provided with suitable means for properly adjusting the relative gas and primary air supplies so as to ensure a vertical series of non-luminous and, as nearly as possible, silent Bunsen flames, of uniform height and character. Above each flame is fixed a hollow fireclay columnal "radiant" perforated in a manner expressly contrived to promote uniform heating of the column throughout, and with each flame rising into the cavity of its particular radiant. Care is taken to prevent any impingement of the inner cone of the flame upon its radiant. The back of the fire is formed by a fireclay slab fixed vertically behind the radiants, which are held in position by means of one slight horizontal iron rod. At a suitable distance above the top of the radiants is fixed a metallic hood or "canopy" by means of which the products of combustion are collected and discharged through the flue vent into the chimney without in any way contaminating the atmosphere of the apartment.

The object of a properly designed fire should be to secure the maxima of radiant and ventilating effects with a minimum of "flue heat," and it is in connection with these aspects of the problem that the need of convenient and

accurate means of measuring the radiant efficiency of the fire has been mostly felt.*

A joint committee appointed in 1907 by the University of Leeds and the Institution of Gas Engineers to investigate gas fires adopted a method (now known as the Leeds method) for determining their radiant efficiencies. It consists essentially in firstly establishing, by thermopile readings, a relation between the intensity of the radiation at a central equatorial area on a hemisphere in front of the fire, and the total radiation received over the whole hemisphere (a relation which will be hereafter referred to as the "distribution factor" of the fire), and then determining, by means of a radiometer, of the water-calorimeter type, designed by Prof. R. H. Smith, the actual number of calories radiated by the fire per hour on to the said equatorial area. The number of such calories multiplied by the "distribution factor" of the fire gives the total energy radiated by the fire per hour, and the relation of this to the total net heat developed by the combustion of the gas in the fire per hour gives the radiant efficiency of the fire.†

This method, whilst perfectly sound in principle, is admittedly open to criticism on the following grounds, namely:—

- (1) The R. H. Smith radiometer is liable to various small indeterminable errors inherent in all such water-calorimeter radiometers, due principally to (a) imperfect absorption of the radiation by its blackened surface, (b) effects of "lag," which, however, if the experimental conditions remain constant, may be disregarded, and (c) the difficulty of carrying out a really satisfactory "blank" experiment to determine the allowance to be made in the actual test for heat gained by the instrument from the surrounding warmer atmosphere.
- (2) It is practically impossible, owing to the large area of the absorbing surface of such a radiometer, to standardise its readings from a known absolute radiation standard.
- (3) The time taken to complete both the radiometer (actual and blank) tests and the 81 thermopile readings required to establish the "distribution

^{*} See also H. James Yates on "Recent Progress in Gas-Fire Science," 'Brit. Assoc." Reports, Birmingham, 1913, pp. 435-9.

[†] A full description of the Leeds method is given in the Committee's First and Second Reports, 'Trans. Inst. Gas Engineers,' 1909, pp. 59-81.

[†] There is certainly a small systematic error in the "blank" test, due to the impossibility of screening the radiometer perfectly from the fire during the blank, the effect of which is to make the ascertained "blank correction" too high. By means of the bolometer we have estimated that, in the case of a 10-inch gas fire, and using a single reflecting screen in front of the radiometer during the Leeds blank test, the error may amount to 0.44 kilogramme-calories per hour on a total centre reading (in the actual test) of 55-60 kilogramme-calories.

factor" is considerable, and there is always a risk of some alteration during the test in the experimental conditions which would affect its result.

(4) There is also perhaps a little uncertainty about the absolute accuracy of the "distribution factor" as determined by the Rubens thermopile used in the Leeds method.

In any case, were the method entirely free from any or all such practical objections, it would still be important to compare its results with those obtained by some independent standard method.

The New Bolometric Method.

The problem of measuring the radiant efficiency of a modern gas fire, such as has been described in the introductory part of our paper, is complicated by the fact that the fire front (i.e., the seat of the radiation) cannot be regarded as a surface of simple geometric form. The seat of the radiation has, in fact, a measurable depth, and, owing to the line of the fire front being often slightly curved, its exterior surface is not always flat.

Again, the hemispherical distribution of the radiation may be disturbed either by absorption or by reflection from projecting surfaces on the casing of the fire. It is necessary to determine, not only the whole radiation emitted by a particular fire, but also its distribution factor, because a proper distribution of the radiant energy is almost as important as its total amount.

The Bolometer and its Advantages.

We propose to substitute for the radiometer-cum-thermopile device in the Leeds method a simple bolometer in which the radiation falling from the fire upon a blackened coil of platinum wire can be deduced from the observed increase in its electrical resistance, the area of the receiving coil being sufficiently small to allow of the instrument being standardised directly from a source of radiation of known intensity.

The principal object in employing a bolometer in place of a thermopile is to secure a greater range of accuracy and sensitiveness, and to facilitate the obtaining of automatic records when required. The sensitiveness of a bolometer is readily varied over a wide range by varying the electric current employed for measuring the resistance. The sensitiveness may also be determined very easily, under any conditions, by observing the deflection produced by inserting a known resistance in the circuit. In using the Rubens thermopile (as in the Leeds method), it is found necessary to attach a reflecting cone to the instrument in order to obtain a deflection of 25 scale divisions with a Paul unipivot galvanometer at a distance of

3 feet from a 10-inch gas fire. The use of a reflecting cone narrows the angular aperture, and introduces some uncertainty with regard to the extent of the source from which the radiation is actually received. The bolometer, when supplied with the current for which it is designed, and employed in conjunction with the same unipivot galvanometer but without any reflecting cone, is found to have a sensitiveness about thirty times as great as the Rubens thermopile with the cone, and could be used at much greater distances from the fire. By adjusting the sensitiveness to a suitable figure in scale divisions per ohm, it is always possible to obtain deflections in the neighbourhood of 90 or 100 scale divisions, which greatly facilitates the accurate determination of the radiation.

Construction of the Bolometer.

The familiar type of bolometer invented by Prof. Langley has a sensitive receiving surface in the form of a grid cut from thin metal foil, and is blackened with smoke black or platinum black. This method of construction was adopted with the object of securing the greatest quickness of action, but it involves extreme fragility and is wanting in constancy. The coating of black invariably deteriorates, and cannot be renewed without altering the constant of the instrument. Constancy is much more important for the present purpose than quickness of action, and fragility would be a serious defect.

A different method of construction was accordingly adopted in our experiments; the delicate grid of the Langley bolometer has been replaced by a coil of platinum wire wound on a thin piece of mica, and coated to an even surface with hard black enamel, which is extremely permanent, and can be cleaned without risk of injury. Two exactly similar coils, each 4 cm. square and of 20 ohms resistance, are mounted back to back on either side of a circular gunmetal box, provided with water circulation, and with suitable covers for the coils, so that either coil can be exposed to radiation or screened. When both coils are screened they are kept at the same temperature as the box, their resistances remain equal, and there is no deflection of the galvanometer, however much the temperature of the box may change. But if one of the coils is exposed to radiation, its temperature and resistance are increased by an amount depending on the intensity of the radiation, and the galvanometer shows a deflection proportional to the increase of resistance, which serves as a measure of the intensity of the incident radiation.

Calibration of the Bolometer.

An instrument of this type can be directly calibrated to give the intensity of the radiation in absolute measure, by observing the magnitude of the electric current required to produce the same rise of temperature, or increase of resistance, as the radiation to be measured. This method has often been adopted, but is not quite satisfactory, on account of the uncertainty of the absorption factor of the surface for radiation, which is one of the commonest sources of error in all measurements of radiation. The constant of the bolometer, giving the intensity of the radiation in terms of increase of resistance, was accordingly determined by comparison with a radio-balance, an instrument specially designed to give total absorption of the radiation.*

In the radio-balance, the radiation to be measured is admitted through a small circular aperture and received in a blackened copper cup, in which the absorption is practically complete. The heat received from the radiation is balanced by absorption of heat due to the Peltier effect in a thermojunction through which a measured electric current is passed. This method is very accurate, but is not well suited for ordinary use outside a physical laboratory, because it requires a sensitive galvanometer for indicating the balance, and a delicate ammeter or potentiometer for measuring the electric current. Nevertheless, a bolometer such as the one herein described can, without risk of fracture of its working parts, be sent to a physical laboratory for comparison with a radio-balance.

The following Table contains all the results for the constant of this particular bolometer obtained by comparison with two different radio-balances, denoted by D and E respectively. Two different sources of

	Date.	Radio- balance.	Temperature of bolometer.	Air.	Source of radiation.	Constant of bolometer.
,,	7. 28 29 3 3	K D D D E D E	21 ·5 21 ·0 15 ·7 17 ·2 17 ·7 18 ·9 18 ·7 20 ·7 18 ·8	22 · 0 21 · 5 18 · 0 18 · 7 18 · 0 18 · 2 18 · 8 19 · 2 21 · 2	Clas fire Focus lamp Clas fire Focus lamp Clas fire Focus lamp Clas fire	27 ·71 27 ·85 28 ·09 28 ·02 27 ·82 27 ·96 27 ·86 27 ·86 27 ·82 27 ·78
	Means		18 -9	19 ·4		K = 27 ·88

Observations of Bolometer Constant K.

^{* &#}x27;Proc. Phys. Soc. Lond.,' vol. 23, pp. 1-34 (1910).

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radiation were employed—(1) a 10-inch gas fire at a distance of 1 metre, (2) a focus lamp of 100 candle power, having a small radiant 1 inch square, at a distance of 30 cm. It was unfortunately impossible to vary the temperature of the laboratory materially, but the temperature of the bolometer was altered 5° or 10° on each occasion, by changing the water circulation, in order to determine the correction for the difference of temperature between the bolometer and the air. The results given for the constant are corrected for the observed difference.

The value of the constant is given as the intensity of the radiation in kilocalories per square foot per hour required to produce an increase of resistance of 1 ohm in the exposed coil of the bolometer. The chief source of error in the comparisons was the uncertainty of temperature of the surrounding air and the walls of the room, which cannot be well avoided in measurements of this kind with a source of large area like a gas fire, since the receiving instrument is necessarily exposed to the air and to radiation from surrounding objects, which may be at different temperatures. The correction for difference of temperature between the air and the bolometer was found to be 0.028 ohm per 1° C., and amounted in some cases to as much as 4 per cent., when the difference of temperature was considerable, but the divergence of the corrected results from the mean in no case reaches 1 per cent., and is generally less than 0.5 per cent.

The Distribution Factor.

The "distribution factor" of a gas fire, or other approximately flat source of radiation, may be defined as the factor by which the normal intensity at a given distance D must be multiplied in order to obtain the total radiation emitted over a hemisphere. If the source is a plain circular disc of uniform intensity and of radius R, the value of the factor given by the theory of radiation for a self-luminous surface, would be simply $\pi(D^2 + R^2)$. Thus, for example, in the case of a plane source 1 foot in diameter, tested at a distance of $9/\pi$ feet, or 34.38 inches, the value of the distribution factor should be 26.58, which is about the value generally obtained for a 10-inch gas fire, tested at this distance, by taking a large number of readings equally distributed over the surface of a hemisphere. In the case of a gas fire the surface is, however, seldom flat, and there are considerable extensions, such as the canopy, which contribute an appreciable fraction of the radiation. The chief uncertainty arises in estimating the distance D. An error of 1 inch in D in the above example would make an error of nearly 6 per cent. in the mathematical formula, and it may be doubted whether this error

can be eliminated in practice by taking observations over a hemisphere of fixed radius.

The obvious method of reducing this uncertainty, especially with a large gas fire, would be to increase the distance. But this introduces some practical difficulties if a large number of readings are to be taken over a hemisphere of large radius. It is doubtful whether an accurate result can be obtained by mere multiplication of readings. Since the deviation of the distribution factor from the theoretical value for a flat surface is evidently small, it would probably suffice to take a few readings at suitably selected angles. It appears from theory, and also from comparison of observations, that the sum of four readings taken at 60° along the equator and meridian, together with the central reading, multiplied by $\pi D^2/3$, (8.6, when $D = 9/\pi$ feet), gives as good an approximation to the total radiation as can be obtained by taking 81 readings. The distribution factor is represented by the sum of the five readings divided by the central reading and multiplied by $\pi D^2/3$.

Effect of Variation of Temperature of Receiver.

The importance of keeping the temperature of the receiver, whether bolometer or thermopile, constant, is best appreciated by taking a case in which this precaution is omitted. If a Rubens thermopile with a Paul indicator (such as is used in the Leeds method) is exposed to a steady source, giving an intensity of 46 kilocalories per square foot per hour, the deflection rises to about 25 mm. in 15-20 seconds, and creeps up to 27.5, a further 10 per cent., in three or four minutes. The deflection then diminishes to about 25 mm. if the exposure is prolonged, on account of rise of temperature of the case, which may amount to 5° or 10° C.

If, now, the hot instrument is screened from the source, or turned towards the wall of the room, which is at a lower temperature, it falls quickly to zero and gradually takes up a negative deflection of 3 or 4 mm. In other words, the rise of temperature of the instrument may produce an effective change of zero equivalent to 10 or 15 per cent. of the deflection. Variations of this magnitude make it impossible to employ the pile with a constant reduction factor for determining the absolute value of the radiation. In using the pile merely for the distribution factor, the errors are not so obvious, but, being systematic, they produce a marked effect on the results, as is shown by the following typical comparison of readings taken with thermopile and bolometer, along the equator in front of a gas fire.

Position	60° West.	о°.	60° East.
Thermopile Bolometer Thermopile	16 ·0	28 · 3	13 ·0
	58 ·2	91 · 2	58 ·0
	15 ·2	22 · 9	18 ·0

The thermopile readings make the distribution appear about 20 per cent. greater on the west than on the east. There is no reason why this should be the case, and the bolometer readings show practically no difference between cast and west. The explanation is that in the case of the thermopile the west readings were taken first, while the deflection was still increasing, whereas the east readings were taken after the instrument had become hot, with the consequent depression of zero. The opposite errors on the two sides tend to neutralise each other to some extent, but the general effect is to reduce all the smaller readings unduly as compared with the central reading, so that the distribution factor obtained with the thermopile may be as much as about 3-5 per cent. too small. This point may be illustrated by reference to the following Table of the "Distribution factor" of the same 10-inch gas fire as determined on several different occasions by means of (1) the bolometer, and (2) a Rubens thermopile.

The Distribution Factor of a 10-inch Gas Fire as determined by-

Bolometer.	Thermopile.
28.23	27.42
28 56	27:55
28 ·65	27.12
28.30	27.55
28.70	27.57
28.16	27.68
27.97	27.52
28.52	27.13
27.81	Man 07-44
28.52	Mean = 27.44
28.47	Ratio = $\frac{28.36}{27.44}$ = 1.034.
	$\frac{10010}{27.44} - 1004$
Mean = 28.36	

Method of Testing a Gas Fire.

It is usually the most convenient method, in testing a gas fire, to mount the bolometer or thermopile on a revolving sector of fixed radius, the centre of which is adjusted to coincide approximately with the centre of the fire. If the radius of the hemisphere over which the bolometer moves is $9/\pi$ feet, or 34.4 inches, as employed in the Leeds method, an error of 1 inch in the adjustment of the sector along the normal will produce an error of 6 per cent. in the central reading.

It is difficult to specify accurately how this adjustment should be made, especially if a radiometer of large receiving surface, such as 1 sq. ft., is employed for the central reading. The Leeds method of testing throws too much weight on the central reading, which is the most uncertain so far as the adjustment is concerned. The reasons for taking four readings at an angle of 60° with the normal are (1) that these readings take very fair account of the variation of distribution in different directions, (2) that the sum of the four readings will be very nearly independent of small errors of adjustment of the sector, and will reduce to about one-third the probable error of adjustment on the central reading.

Automatic Records.

It is possible with the bolometer to obtain automatic records in ink on a large scale, which are useful in recording the progress of a test, or showing the effect of variation of conditions. The scale is readily varied from 10 to 40 cm. per ohm. The reading obtained with a 10-inch gas fire at a distance of 3 feet is generally between 1.5 and 2 ohms with the bolometer already described. This reading would correspond to a vertical height of 15 to 80 cm. on the record according to the scale employed. The smaller scale is quite sufficient for an ordinary test, but the larger scale is useful in investigating small corrections, due to variation of temperature of the room or similar causes. Readings can be taken more quickly with an indicator such as the unipivot galvanometer already mentioned, but the recorder has the advantage that its scale is more accurate and uniform, and that it is easier to see when the conditions of observation are satisfactorily steady.

Radiant Efficiency of a Gas Fire.

In conclusion, we may tabulate the results of a series of determinations of the radiant efficiency of a 10-inch gas fire working on London coal gas of average net calorific value 32.88 K.C.Us. per cubic foot at N.T.P., with an average consumption of 24.25 cu. ft. per hour at N.T.P., supplied to the fire at a constant pressure of 1.9 inches (water gauge) above the barometric pressure.

Date.	Barometer.	Dry gas consumption per hour at N.T.P.	Net calorific value dry gas K.C.U.'s per cub. ft. at N.T.P.	Radiant efficiency.
1914.	mm.	cub. ft.	*	per cent.
Dec. 9	750 · 3	24 .00	132 0	44.8
, 10	752 ·5	24 ·49	181 .0	45 0
, 11	746 · 1	24 .25	180 -6	43 ·2
, 14	782 -7	23 .78	130 · 2	4 6 O
,, 16	748 •4	24 ·19	131 -8	46 6
17	761 ·1	24 .77	182 -8	44 •6
"	764 -7	24 .49	132 ·8	44 6
1	763 •2	24 .51	181 .7	45 5
	763 •2	24 .26	131 .7	45 .5
, 18	751 4	28 -82	130 '6	44 0
	Chaldran - 11th mattersons service (100)		Mean	45 ·0

The testing room was a laboratory 38 ft. \times 32½ ft. \times 15 ft. high, the temperature of which varied only between 14° and 17° C. during the various tests. The fire was mounted on a special stand, with its flue outlet under a large hood communicating with a chambered wall and chimney which gave a sufficient draught to prevent any of the products of combustion getting into the room.

The five bolometer readings in each test were taken at radial distances of 34.4 inches from the centre of the fire: one central reading and four other readings in positions 60° N., S., E., and W. respectively, of the central position. A mean "distribution factor" of 28.36, as determined for the said fire, was used in the calculations.

Finally, the authors desire to thank Messrs. A. Forshaw, M.Sc., and S. Farrar, B.Sc., for their assistance in connection with the experimental part of the investigation.

The Laws of Series Spectra.

By J. W. Nicholson, M.A., D.Sc., Professor of Mathematics in the University of London.

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Several theories of the production of series spectra have been given in recent years, and it has become apparent that no further real progress can be made in the interpretation of spectra until the true form of the series relations is known more accurately. Various formulæ, such as those of Ritz and Hicks, fit the measured wave-lengths almost equally well, and all demonstrate at least the approximate truth of two fundamental results: (1) that the Diffuse and Sharp series tend to the same limits, and (2) that the difference between the limiting wave-numbers of the Sharp and Principal series is the wave-number of the first Principal line. The first is now usually taken as proved, but no formula has yet made it evident that the second—the Rydberg-Schuster law—is more than a close approximation. One of the objects of this paper is to show that it is an absolute law. Another fundamental question, on which different opinions are held, is that of Rydberg's constant. Hicks* has concluded that this constant may be slightly different in the various series produced by helium. According to Bohr's theory of spectra+ it should be an absolute constant for all the ordinary helium series, but different from the hydrogen constant by a calculable amount. The results of this paper tend to show that the constant for arc spectra is absolute, and has the value 109679.22, recently determined by Curtist for hydrogen only, on the International scale of wave-lengths.

The formula for any series, whether Diffuse, Sharp or Principal, is

$$\nu_m = A - N/D_m^2, \tag{1}$$

where ν is the wave number of a line, N is Rydberg's constant, and D_m is a function of an integer m. According to the Hicks formula,

$$D_m = m + \mu + \alpha/m, \tag{2}$$

where μ and α are constants. The Ritz formula usually quoted makes

$$D_m = m + \mu + \alpha/m^2, \tag{3}$$

and it has been decided that (3) is not so good as (2), although α is usually

^{* &#}x27;Phil. Trans.,' A, vol. 210, p. 111, 1.

[†] Phil. Mag.,' vol. 26, pp. 1 and 476 (1913).

^{‡ &#}x27;Roy. Soc. Proc.,' vol. 90, p. 605 (1914).

so small that their difference is not very appreciable. This inferiority nevertheless exists. But the formula on which Ritz* really relied was of the form

$$\nu_m = A - N / \{m + \mu + \alpha (A - \nu)\}^2, \tag{4}$$

not expressing ν explicitly as a function of m, so that the failure of (3), which is only an approximation, is not a conclusive test of Ritz' formula.

This paper will indicate that (4), although unsatisfactory, is probably the best form for this number of constants, without implying, however, that Ritz' theoretical foundation for the formula is correct. Into the question of the origin of series we shall not enter.

Hicks has made the interesting suggestion that

$$D_m = m + \mu + \alpha/(m + \mu) + \alpha/(m + \mu) + ...,$$
 (5)

an infinite continued fraction, whose value is

$$D_m = \frac{1}{2}(m+\mu) + \sqrt{\left[\left(\frac{1}{2}(m+\mu)\right)^2 + \alpha\right]}.$$
 (6)

The relation between (5) and (2) is very similar to that between Ritz' formula (4) and its approximation.

The conclusions reached in the paper are the result of a consideration of several different spectra which are known with sufficient experimental accuracy to enable a discrimination between the formulæ to be made. In the paper, however, only the spectrum of helium will be dealt with, for it is peculiarly suitable on account of the general accuracy of its abundant series, and the especial accuracy of the first lines of the series, measured by Lord Rayleigh‡ and by Eversheim.§ Moreover, theories of atomic structure are becoming definite in the case of helium, and can only be tested by a more intimate knowledge of the nature of its spectrum. Perhaps at this point we may emphasize the urgent need, to the theoretical spectroscopist, of interferometer measurements of four or five successive lines in any helium series.

The very complete study of the helium spectrum made by Hicks|| does not include the measurements of Eversheim, which are according to the International scale of wave-lengths. This scale must be used in any accurate discussion of spectral formulæ. At the same time, wave-lengths reduced to vacuo must be employed. The reductions to vacuo may be effected by the tables published by Kayser, and they have been applied to all the wavelengths studied below.

The main novelty in the treatment consists of a method for the accurate

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* 'Ann. der Phys.,' vol. 25, p. 660 (1908).
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^{† &#}x27;Phil. Trans.,' A, vol. 210, p. 60 (1910).

^{† &#}x27;Phil. Mag.' (6), vol. 15, p. 548 (1908).

^{§ &#}x27;Kayser's Handbuch,' vol. 5, p. 520.

^{||} Loc. cit.

^{¶ &#}x27;Handbuch der Spectroscopie,' vol. 2, p. 576.

determination of the limits of series, which requires, for its application, a preliminary formula, for example of the Hicks type, for the expression of the series.

The Diffuse or First Subordinate Series of Helium.

Hicks has represented this series with great accuracy by the formula

$$\nu = 29222 \cdot 595 - 109689 \cdot 2/\{m + 0.996347 + 0.002200/m\}^2. \tag{7}$$

The lines are doublets, and the formula relates to their more refrangible components.

In the following Table are the wave-lengths (λ) and wave numbers (ν) of the lines of this series. The first two are Eversheim's, and the others are Runge and Paschen's, reduced to the International scale by the corrections published recently by Kayser.* All have been reduced to vacuo.

m,	λ in Å.	$\nu=10^8\lambda^{-1}.$	m.	λ in Å.	$\nu = 10^9 \lambda^{-1}.$
2	5877 -240	17014 -789	9	3555 440	28125 -912
3	4472 .724	22857 .740	10	3581 486	28316 689
4	4027 308	24880 .479	11	3518 485	28461 .766
5	3820 .664	26173 .459	12	3499 .614	28574 .581
6	3706 034	26983 :021	18	3488 .704	28668 941
7	3635 258	27508 :362	14	3479 934	28736 170
8	3588 280	27868 .503	15	8472 .764	28795 .506

The last figures in λ are not all exact, and, in certain cases, the errors, which are larger than were estimated by Runge and Paschen, amount to 1/100 of an Ångstrom unit. In the following investigation, however, where the limit is calculated from every pair of successive lines, the mean must be very accurate if the errors in the lines are not systematic.

The Hicks formula shows that they can be represented by

$$\nu_m = A - N/(m + \delta + 1)^2,$$
 (8)

where δ never exceeds 0.004. If this be expanded

$$\nu_m = A - \frac{N}{(m+1)^2} \left[1 - \frac{2\delta}{m+1} + \frac{3\delta}{(m+1)^2} \dots \right].$$

The fourth term of this very convergent series is $3N\delta^2/(m+1)^4$. Since N is about 10⁵, this cannot exceed

$$3.10^{6}.16.10^{-6}.3^{-4} = 0.06.$$

even when m=2. If we take all the lines beyond m=3, it cannot exceed 0.007, so that for all these lines

$$\nu_m = A - N/(m+1)^2 + 2N\delta/(m+1)^3;$$

* 'Handbuch der Spectroscopie,' vol. 6, p. 891.

or
$$(m+1)^{3} \nu_{m} = A (m+1)^{3} - N (m+1) + 2 N \delta,$$

$$(m+2)^{3} \nu_{m+1} = A (m+2)^{3} - N (m+2) + 2 N \delta,$$

$$(m+3)^{3} \nu_{m+2} = A (m+3)^{3} - N (m+3) + 2 N \delta.$$
and
$$A = \frac{(m+2)^{3} \nu_{m+1} - (m+1)^{3} \nu_{m} + N}{(m+2)^{3} - (m+1)^{3}}.$$

$$(9)$$

If the value of N were known, this formula would permit a determination of the limit of the series from any pair of consecutive lines. Actually, the exact value of N is one of the objects of the investigation, but we know that it cannot differ greatly, whether on a definite theory such as Bohr's, or on the results of the calculations of Hicks, from Curtis' value for hydrogen. We may therefore write $N = 109679 \cdot 22 + \delta N$, where δN represents the divergence of the value from that of Curtis, and treat δN as a small unknown magnitude. The calculated limit for any two lines is then of the form $C + B\delta N$, where C and B are numerical, and B is a very small coefficient, of order, as appears later, about 10^{-4} . A series of values of this type are then obtained, and their mean, taken in accord with the usual methods, must be much more accurate than the value of the limit calculated, by the ordinary methods, by fitting an empirical formula to the leading lines of the series. For, in the present method, every line, beyond say m=3, will be used twice.

This final mean limit involves δN as an unknown quantity, and, in fact, the basis of the method consists of converting the ordinary uncertainty regarding the limit into a definite function of the uncertainty in the value of N. In this way it becomes possible to proceed, without a more definite determination of the limit, just as though that limit were accurately found, for the degree of uncertainty is known as an exact function of δN .

One or two remarks may be made at this point. Although a Hicks formula is our starting point, the small systematic deviations given by any Hicks formula for the higher lines do not enter into the calculated sequence of limits, whose mean is finally taken. They would be detected, if present, by a systematic change in the calculated limits, and, as pointed out later, when these are calculated this effect does not occur. On the other hand, from the mathematical point of view, the binomial development used above does not admit of their occurrence, being remarkably independent, in its final results, of small changes in the value of $m + \mu$ adopted.

The small differences between our limits and those of Hicks are not entirely due to the use of International units.

The Sharp or Second Subordinate Series of Helium.

The Hicks formula for this series is

$$\nu_m = 29222 \cdot 696 - 109719 \cdot 6 / \{m + 0.705092 - 0.013408 / m\}^2, \tag{10}$$

and the lines, corrected to the International scale and for the refractive index of air, are shown in the next Table. The first two are Eversheim's absolute measurements.

m.	λ.	14.	m.	λ.	ν.
2	7067 -128	14150 -028	9	3563 973	28058 -572
8	4714 .448	21211 .889	10	8587 804	28266 120
4	4121 963	24260 284	11	8518 .816	28422 .688
5	3868 -587	25849 564	12	8503 -802	28544 '496
6	3738 -894	26781 690	13	3491 .602	28640 146
7	3652 .991	27874 .826	14	8482 482	28715 562
8	3600 -329	27775 -287		}	

The Hicks formula is of the type

$$\nu_m = A - N/(m + 0.7 + \delta)^2, \tag{11}$$

where, after m=3, δ never exceeds 0.004, so that the preceding method can be applied, giving

$$A = \frac{(m+1.7)^3 \nu_{m+1} - (m+0.7)^3 \nu_m + N}{(m+1.7)^3 - (m+0.7)^3}.$$
 (12)

The Principal Series.

In this case the Hicks formula is

$$\nu = 38453 \cdot 347 - 109666 \cdot 2/\{m + 0.929442 + 0.007792/m\}^{2}.$$
 (13)

Only the first line has been measured by an interference method. The probable correction required to reduce it to vacuo has been found by interpolation from Kayser's Tables as 2.53 Å.U. Paschen gives its wavelength as 10830.30 Å.U., measured by the interferometer.

m.	λ.	ν.	m.	λ.	ν.
1	10832 -68	9231 ·198	8	2764 600	86171 .595
2	8889 ·715	25708 -822	7	2728 -965	36711 -188
8	8188 -608	81861 -695	8	2696 914	87079 -418
4	2945 -954	88944 .858	9	2677 .880	37342 967
5	2829 -879	85387 -197	10	2663 976	87537 869

^{*} Trans. Intern. Union Solar Research, Bonn, 1913.

Beyond m=2 even, we may take the denominator in Hicks' formula as $(m+0.930+\delta)^2$, where δ is of order 0.002 at most. Then, for m=3,

$$3N\delta^{2}/(m+0.93)^{4}=0.005$$

and is negligible. Thus we may write, beyond m = 2,

$$A = \frac{(m+2.93)^3 \nu_{m+2} - (m+1.93)^3 \nu_{m+1} + N}{(m+2.93)^3 - (m+1.93)^3}.$$
 (14)

The next section exhibits the results of these calculations.

Limits of the Series.

For the Diffuse series, using lines beyond m = 3, successive values of the limits are

$$A = 29223 \cdot 478 + \delta N/91, \qquad A = 29223 \cdot 530 + \delta N/127,$$

$$29223 \cdot 577 + \delta N/169, \qquad 29223 \cdot 671 + \delta N/217,$$

$$29223 \cdot 072 + \delta N/271, \qquad 29224 \cdot 412 + \delta N/331,$$

$$29224 \cdot 429 + \delta N/397, \qquad 29224 \cdot 085 + \delta N/469,$$

$$29223 \cdot 354 + \delta N/547, \qquad 29224 \cdot 149 + \delta N/631.$$
(15)

No value of δN can be found which makes the general deviations from equality any smaller than they are for the calculated parts at present—a first indication that $\delta N = 0$.

If δN exists the other portions should become progressively larger, and this does not occur either here, or with the Sharp and Principal series.

The mean value is

$$A = 29223.776 + 0.004416 \delta N, \tag{16}$$

and differs only slightly from each individual value. As there are 10 of these we may attach considerable accuracy to the mean. SN denotes the increase of the value of N beyond that of Curtis. It is noteworthy that the value chosen for N makes only a minute difference in the limit, if the variations of N are of the order hitherto suggested.

The application of the same process to the Sharp series gives the values

$$A' = 29225 \cdot 350 + 0 \cdot 01229 \, \delta N', \qquad 29224 \cdot 386 + 0 \cdot 00865 \, \delta N', \\ 29224 \cdot 170 + 0 \cdot 00642 \, \delta N', \qquad 29223 \cdot 373 + 0 \cdot 00495 \, \delta N', \\ 29224 \cdot 154 + 0 \cdot 00393 \, \delta N', \qquad 29223 \cdot 648 + 0 \cdot 00320 \, \delta N', \\ 29223 \cdot 279 + 0 \cdot 00265 \, \delta N', \qquad 29226 \cdot 665 + 0 \cdot 00224 \, \delta N', \\ 29224 \cdot 514 + 0 \cdot 00191 \, \delta N', \qquad 29217 \cdot 241 + 0 \cdot 00165 \, \delta N'. \end{cases}$$

$$(17)$$

The general mean is

$$A' = 29223.678 + 0.00479 \delta N', \qquad (18)$$

but a more accurate value will be obtained by attaching weights of ½ to the first, eighth and tenth values, which differ considerably from the others.

We notice that in the 10 values of A' or of A, there is not a systematic increase or decrease, whether δN , $\delta N'$ are zero or not. This illustrates the remark on an earlier page that the method does not involve the systematic small deviations usually given by a Hicks formula for the higher lines (in order of m) in any series.

The resulting weighted mean is

$$A' = 22223.780 + 0.00468 \delta N'. \tag{19}$$

More exhaustive treatment does not appreciably alter this value.

The Principal series, treated in the same way beyond m = 3, gives the values

$$A'' = 38451 \cdot 831 + 0 \cdot 0169 \delta N'', 38454 \cdot 435 + 0 \cdot 0113 \delta N'', 38454 \cdot 052 + 0 \cdot 0080 \delta N'', 38455 \cdot 155 + 0 \cdot 0060 \delta N'', 38457 \cdot 993 + 0 \cdot 0031 \delta N'', 38456 \cdot 579 + 0 \cdot 0038 \delta N'', 38457 \cdot 993 + 0 \cdot 0031 \delta N'',$$

The general mean is

$$\mathbf{A}'' = 38454.801 + 0.00768\delta N'', \tag{21}$$

from which we see that if $\delta N''$ is not large, the only bad values are the first and last. Now the first pertains to the lines most readily measured, and we must conclude that the strict applicability of the method has not commenced at this stage, so that the first two lines at least should be weighted on this account. A similar error of opposite sign does not appear in the second value, as it should if an error of measurement accounted for the discrepancy in the first value, according to the method used for the calculation. The divergencies in the first and last values practically balance, so that the general mean must be nearly accurate, so far as casual observational errors are concerned. By attaching weights 1, 2, 3, 4, 5, 6 to the first six values, corresponding roughly to the degree to which the formula is applicable, and a weight 1 to the last value, we shall obtain a mean nearly free from errors in formula.

The result is
$$A'' = 38454.943 + 0.00622 \delta N''$$
, (22)

and this result must possess considerable accuracy, beyond, in fact, the accuracy of individual lines.

We may now consider the values of δN , $\delta N'$, $\delta N''$. The limits are

$$\begin{array}{l}
 A = 29223.776 + 0.004416 \delta N \text{ (Diffuse),} \\
 A' = 29223.780 + 0.00468 \delta N' \text{ (Sharp),} \\
 A'' = 38454.943 + 0.00622 \delta N'' \text{ (Principal).}
 \end{array}$$
(23)

If Curtis' value is used, or if N is an absolute constant for arc spectra, $\delta N = \delta N' = \delta N''$, and A = A' with extraordinary closeness, so that the Diffuse and Sharp limits are identical. The simple Hicks formulæ make them differ by 0.1. Moreover, the Rydberg-Schuster law gives us the wave number of the first Principal line,

$$\nu = 38454.943 - 29223.780 = 9231.163', \tag{24}$$

against the practical value 9231·198. The agreement is almost exact, and that both these laws should be fulfilled so exactly at the same time is a convincing reason for belief in both, and also in the fact that Curtis' value pertains to helium. Even the minimum value of δN required by Bohr's theory, if the arc spectrum of helium behaved like the spark series discovered by Fowler, is only 44·8, but this makes a serious difference in the limits of the Diffuse and Sharp series. Since, however, no method has been suggested by which the theory can produce the arc spectrum of helium, and such a suggestion appears to be impossible,* we cannot now go into this question. But attention must be called to the extreme sensitiveness of this mode of testing the Rydberg-Schuster law, if many lines in the series are known.

After the proof in later sections that $\delta N=0$, it is possible to say that the laws of limits are exact. The actual limits deduced are not quite those of Hicks, which give a difference of about 0.4 in the Rydberg-Schuster law. Such a difference can be proved not to arise from the difference between Rowlands' and the International scale, which can only account for a quarter of the effect. The method of the paper, therefore, definitely tends to confirm the Rydberg-Schuster law, which has now been shown to be correct to six significant figures in either limit.

The Series Formula.

The present section is designed to show that three ideas—the Rydberg-Schuster law, Curtis' value of the universal constant, and Rydberg's hypothesis that wave numbers of series lines are functions not of an integer m, but of $m + \mu$, where μ is the 'phase' of the series—are intimately bound together, and that if we assume any one of them, the others follow as necessary consequences of a strict examination of any well-measured spectrum. In the opinion of the writer, this fact is a conclusive proof for the truth of all three. We shall examine, in the most minute manner allowed by the measurements, the Sharp series of helium, with the preliminary remark that the results

obtained are not peculiar to helium. The idea assumed will be the Rydberg-Schuster law.

The Sharp series has the form

$$\nu_m = A' - N'/\rho_m^2,$$

where ρ_m is of an unknown form at present. If N' = 109679.22 + δ N, the form becomes

$$\nu_m = 29223.780 + 0.00468 \delta N' - (0.109679.22 + \delta N') / \rho_m^2, \tag{25}$$

where

 $\nu_2 = 14150.028, \quad \nu_3 = 21211.389,$

 $\nu_4 = 24260.284$

the first two being the extremely accurate measurements of Eversheim.

By the Rydberg-Schuster law, ν_1 is minus the wave number of the first principal line, or

$$\nu_1 = -9231.198$$

The corresponding values of ρ_m can be calculated from (25), and to the first order in δN , become

$$\rho_{1} = 1.688836 + 0.0759 \,\delta N,
\rho_{2} = 2.697438 + 0.01187 \,\delta N,
\rho_{3} = 3.699824 + 0.01578 \,\delta N,
\rho_{4} = 4.700763 + 0.01921 \,\delta N.$$
(26)

Being mainly founded on interference measurements, and on the calculation of close limits from every pair of later lines, these values are more accurate than any previously used in series calculations.

• We may test, in turn, the various forms which have been suggested for ρ_m , treating δN as a small unknown quantity. The only suggestions regarding the existence of δN are (1) that it exists (or may exist) as a small positive quantity, not greater than about 130 in helium (Hicks), and (2) that it has the value + 44.8 required by Bohr's theory.

We shall begin with the two-constant formulæ for ρ_m . Hicks has suggested that the form

$$\rho_m = m + \mu + \alpha/m \tag{27}$$

is exact. If this be the case,

$$\begin{array}{rcl}
1 + \mu + \alpha &=& 1.688836 + 0.05759 \,\delta \text{N}, \\
2 + \mu + \alpha/2 &=& 2.697438 + 0.041187 \,\delta \text{N}, \\
3 + \mu + \alpha/3 &=& 3.699924 + 0.041578 \,\delta \text{N},
\end{array}$$

and the solution of these equations yields

$$\delta N = 194.3, \tag{28}$$

a value too large for either of the suggested changes in N. It is five times Bohr's value.

The approximate Ritz form is

$$\rho_m = m + \mu + \alpha/m^2,$$

and when treated in the same manner for the first three lines, which are sufficiently accurately measured to determine δN precisely, yields

$$\delta N = -255 \cdot 2, \tag{29}$$

This is both large and negative, and the formula is therefore not so good as that of Hicks. This fact is in agreement with ordinary experience, which shows that the formula is also less satisfactory in other respects.

Hicks has suggested

$$\rho_m = m + \mu + \alpha/(m + \mu) + \alpha/(m + \mu) + \dots,$$

which is equivalent to

$$\rho_m = \frac{1}{2} (m + \mu) + \frac{1}{2} \sqrt{\{(m + \mu)^2 + 4\alpha\}}. \tag{30}$$

The application of this formula is more complicated, and need not be given in detail. It leads to the value

$$\delta N = 776, \tag{31}$$

so that the formula cannot be entertained.

The proper Ritz formula makes

$$\rho_m = m + \mu + \beta (A' - \nu_m) = m + \alpha + \gamma \nu_m \quad \text{(say)}, \tag{32}$$

dependent on the wave number explicitly as well as implicitly.

If this be employed,

$$1 + \alpha - 9231 \cdot 198 \gamma = \rho_1,$$

$$2 + \alpha + 14150 \cdot 028 \gamma = \rho_2,$$

$$3 + \alpha + 21211 \cdot 389 \gamma = \rho_3,$$

where ρ_1 , ρ_2 , ρ_3 , are given by (26). This leads on solution to

$$\delta N = 86.7. \tag{33}$$

This value is nearer the accepted limits of possible variation of N, and the formula is therefore better than any of those preceding.

We shall not give the further discussion of the formula, but it is sufficient to say that if this value of δN is used and the other constants calculated, the ensuing wave numbers for the lines corresponding to m=4 and m=5 are not quite satisfactory. They are, however, better than those given by any of the preceding formulæ. Another mode of attack is to calculate the value of δN furnished by the lines m=2, 3, 4, which are measured with sufficient accuracy. It becomes $\delta N=53\cdot 1$, differing somewhat from the preceding value, but very close to zero in comparison with the others. A variation of this amount in N has little effect on later lines, and we may conclude that a true

Ritz formula, with N = 109740.0, is remarkably accurate for the Sharp series of helium, but that it does not obey the Rydberg-Schuster law accurately. This utility of the Ritz formula is significant later, for it involves ρ_m as a function of $m + \mu$ rather than of m.

Many other two-constant laws for ρ_m have been examined, but none are satisfactory, the test of a satisfactory law being that δN does not exceed a certain rough value, and that it shall be at least approximately the same whether calculated from m=1, 2, 3, or m=2, 3, 4. The conclusion has been reached that no formula with only two constants in ρ_m can obey the Rydberg-Schuster law, and represent the Sharp series accurately. It is, in fact, a matter of practical experience among spectroscopists that the deviations given by all such laws, however small, are systematic for the lines with the higher values of m. We now see that this is not due to uncertainty about the limit of the series.

One of these remaining laws, however, is of special interest later. If we write

$$\rho_m = m + \mu + \alpha/(m + \mu), \tag{34}$$

we have a two-constant law satisfying Rydberg's opinion that $(m + \mu)$ is the important parameter in ρ_m . This makes

$$(1+\mu)^2 + \alpha = (1+\mu)\rho_1,$$

$$(2+\mu)^2 + \alpha = (2+\mu)\rho_2,$$

$$(3+\mu)^2 + \alpha = (3+\mu)\rho_3,$$

$$\mu = \frac{2\rho_2 - \rho_1 - 3}{2 + \rho_1 - \rho_2} = \frac{3\rho_2 - 2\rho_3 - 5}{2 + \rho_2 - \rho_3}.$$

or

The value of δN is therefore given by an easy calculation, and becomes $\delta N = 830$.

The formula is therefore not a good one, and when we compare it with that of Ritz, the best yet treated, we reach an interesting conclusion. For the true Ritz formula has for its second approximation

$$\rho_m = m + \mu + \beta / (m + \mu)^2; \tag{35}$$

and if the true form is

$$\rho_m = m + \mu + \alpha/(m + \mu) + \beta/(m + \mu)^2,$$

then α is less important than β . This conclusion is confirmed later.

Three-Constant Formulæ for
$$\rho_m$$
.

If any of the preceding formulæ are first approximations to the truth, their systematic generalisation by the addition of more constants should lead to better results. In this section, we shall treat the Hicks formula, and the

formula last quoted, in this manner, and it will become apparent that a definite conclusion as regards these formulæ can be reached. But this conclusion is actually a general one as regards three- or four-constant formulæ, for many have been tried which we have not space to mention. Throughout the work one formula has stood out with special excellence, and the contingent circumstance that it preserves Rydberg's absolute constant is a further indication of its truth. In view of the especial accuracy of the lines which are used, the success of this formula is more significant than those of formulæ applied to lines of less accuracy in previous investigations.

The first generalisation of the Hicks formula is

$$\rho_m = m + \mu + \alpha/m + \beta/m^2, \tag{36}$$

and if it be applied to the first four lines,

$$1 + \mu + \alpha + \beta = \rho_1,$$

$$2^3 + 2^2 \mu + 2 \alpha + \beta = 2^2 \rho_2,$$

$$3^3 + 3^2 \mu + 3 \alpha + \beta = 3^2 \rho_3,$$

$$4^3 + 4^3 \mu + 4 \alpha + \beta = 4^2 \rho_4.$$

The elimination of μ , α , β , can be performed at once by a well known theorem of algebra, to the effect that if r and p are integers, and a and b any quantities,

$$(a+pb)^{r} - \frac{p}{1} \{a + (p-1)b\}^{r} + \frac{p(p-1)}{2!} \{a + (p-2)b\}^{r} - \dots = 0 \quad \text{if } r < p$$

$$= b^{p}r! \text{ if } r = p.$$

$$(37)$$

In particular, choosing a = b = 1, p+1 = n,

$$n^{r} - \frac{n-1}{1!}(n-1)^{r} + \frac{(n-1)(n-2)}{2!}(n-2)^{2} - \dots = 0 \quad \text{if } r < n-1$$

$$= n-1! \text{ if } r = n-1.$$
(38)

In the present case n = 4 and we find

$$4^{2}\rho_{4}-3.3^{2}\rho_{8}+3.2^{2}\rho_{2}-\rho_{1}=6.$$

Substituting the values in (26), we find

$$\delta N = 165.8, \tag{39}$$

which is better than the preceding value with the simpler formula, but nevertheless not good. Any formula must be expected to give rather a better value when it contains an extra constant.

If we add yet another constant, and write

$$\rho_{m} = m + \mu + \alpha/m + \beta/m^{2} + \gamma/m^{3}, \qquad (40)$$

then δN is determined by

$$5^{3}\rho_{5}-4.4^{3}\rho_{4}+6.3^{3}\rho_{3}-4.2^{3}\rho_{2}+\rho_{1}=4!=24,$$

and substitution of the values in (26) with the addition of $\rho_b = 5.701324 + 0.04169 \, \delta N$, yields $\delta N = 20.4$. It is evident, therefore, that with the addition of more constants to the Hicks formula, δN is converging to a small value. The values to be expected are zero or 44.8 (Bohr), but the convergence in the case of the Hicks formula is evidently slow, and the number of constants already contained, which is just sufficient to bring δN into the neighbourhood of the expected values, indicates that the formula is not of the best type. In other words, although ρ_m must be capable of development in the form of a series like (40), in descending powers of m, the development is not convergent enough for the smaller values of m. A development in some other inverse power is required, and Rydberg's theory is at once suggested, according to which

$$\rho_m = m + \mu + \alpha/(m + \mu) + \beta/(m + \mu)^3 + \dots, \tag{41}$$

where the coefficients α , β , ..., decrease more rapidly than in the Hicks form, is the natural form of ρ_m . We have already tried the case in which only α is retained. It gives $\delta N = 830$. The accompanying value of the phase μ is found to be

$$\mu = 0.7282$$

The comparative success of the true Ritz formula indicates that Rydberg's formula is on the right lines.

Absolute Character of the Rydberg Constant.

We may now retain another constant and write

$$\rho_{m} = m + \mu + \alpha/(m + \mu) + \beta/(m + \mu)^{2},$$

$$(1 + \mu)^{3} + \alpha (1 + \mu) + \beta = (1 + \mu)^{3} \rho_{1},$$

$$(2 + \mu)^{3} + \alpha (2 + \mu) + \beta = (2 + \mu)^{3} \rho_{2},$$

$$(3 + \mu)^{3} + \alpha (3 + \mu) + \beta = (3 + \mu)^{2} \rho_{3},$$

$$(4 + \mu)^{3} + \alpha (4 + \mu) + \beta = (4 + \mu)^{3} \rho_{4}.$$

Elimination of α and β from the first three equations gives the quadratic for μ ,

 $\mu^{2} \left\{ \rho_{3} + \rho_{1} - 2 \rho_{2} \right\} + \mu \left\{ 6 \rho_{3} - 8 \rho_{2} + 2 \rho_{1} - 6 \right\} + \left\{ 9 \rho_{3} - 8 \rho_{2} + \rho_{1} - 12 \right\} = 0, \quad (42)$ and from the last three.

$$\mu^{2} \left\{ \rho_{4} - 2\rho_{8} + \rho_{2} \right\} + \mu \left\{ 8\rho_{4} - 12\rho_{8} + 4\rho_{2} - 6 \right\} + \left\{ 16\rho_{4} - 18\rho_{8} + 4\rho_{2} - 18 \right\} = 0. \tag{43}$$
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A value of δN must be selected, so that these equations have a root in common.

In the preliminary solution we may neglect the portions of ρ_1 , ρ_2 , ..., dependent on δN , which are in any case small. The first quadratic then becomes

$$0.006216 \mu^2 + 2.002888 \mu - 1.407742 = 0$$

and its solution is

$$\mu = 0.700133. \tag{44}$$

If the terms in δN are included, μ will be altered by an amount $\delta \mu$, where it is easily shown that

$$\delta\mu \left\{ 2\mu \left(\rho_{8} + \rho_{1} - 2\rho_{2}\right) + 6\rho_{3} - 8\rho_{2} + 2\rho_{1} - 6 \right\} \\
= -(\mu + 1)^{2} \delta\rho_{1} + 2(\mu + 2)^{2} \delta\rho_{2} - (\mu + 3)^{2} \delta\rho_{3},$$

where $\delta \rho_1 = 0.05759 \, \delta N$, $\delta \rho_2 = 0.041187 \, \delta N$, $\delta \rho_8 = 0.041578 \, \delta N$, and, finally,

$$\mu = 0.700133 + 0.043227 \,\delta \text{N}. \tag{45}$$

The second quadratic is, without terms in δN ,

$$0.001447 \mu^2 + 2.002032 \mu - 1.405128 = 0$$
;

and, solving in the same manner,

$$\mu = 0.700149 + 0.043898 \, \text{SN}. \tag{46}$$

These two values are identical if

$$\delta N = -2.38. \tag{47}$$

This is the best result yet obtained, and the improvement made by the addition of one more constant is remarkable. δN is now well within the limits of previously suggested variation of N, and it is almost exactly zero, suggesting that zero is its actual value. Moreover, the calculated value of μ becomes $\mu = 0.700056$.

This suggests that μ is converging to the value 0.7 exactly, in other words, that it is a very simple fraction, while δN is converging to zero. This would be in accordance with views expressed by Halm.*

There is a strong case for further investigation, and we therefore employ a four-constant formula to fit the first four values of ρ_m . Thus we write

$$\rho_m = m + \mu + \alpha/(m + \mu) + \beta/(m + \mu)^3 + \gamma/(m + \mu)^3$$
 (48)

and find that μ is then a solution of the cubic

$$\mu^{3}(\rho_{4}-3\rho_{3}+3\rho_{3}-\rho_{1})+3\mu^{3}(4\rho_{4}-9\rho_{8}+6\rho_{3}-\rho_{1}) +3\mu(16\rho_{4}-27\rho_{8}+12\rho_{2}-\rho_{1}-8)+64\rho_{4}-81\rho_{8}+24\rho_{8}-\rho_{1}-60)=0.$$
(49)

^{* &#}x27;Roy. Soc. Edin. Trans.,' vol. 41 (1906).

Neglecting terms in SN, this becomes

$$0.004769 \,\mu^3 + 0.001284 \,\mu^2 - 6.007860 \,\mu + 4.202764 = 0$$

whence

$$\mu = 0.699922$$

The convergence to the value 7/10 is still evident. If we include the terms in δN , the result is

$$\mu = 0.699922 + 0.0001598 \delta N. \tag{50}$$

At the same time, γ is found to be so small that it is of no importance beyond m = 1. The application of the four-constant formula to the lines m = 2, 3, 4, and 5 would therefore lead to the value in (46),

or
$$\mu = 0.700149 + 0.00003898 \, \delta N$$
.

The value of δN for a four-constant formula is therefore obtained by identifying the last two values. It becomes

$$\delta N = +1.87, \tag{51}$$

or almost precisely zero again. There can be no doubt now that the value given by Curtis is absolutely correct for helium as well as hydrogen, and that, the Rydberg form is the proper development for ρ_m —proper, of course, only in the sense of being most natural. For the more lines we use, the more definitely does δN converge to zero. The mean of the last two values is -0.25, which is quite negligible.

The mean value of μ is now, from the last two values,

$$0.700035 + 0.0001208 \delta N$$
, or 0.700005 .

and that its value is exactly 0.7 cannot be doubted.

If we now, using the greatest possible accuracy, adopt $\mu = 0.7$, $\delta N = 0$,

$$\rho_m = m + \mu + \alpha/(m + \mu) + \beta/(m + \mu)^2 + \gamma/(m + \mu)^3, \tag{52}$$

we find, after some reduction,

$$\alpha = 0.018546$$
, $\beta = -0.077181$, $\gamma = 0.02276$,

the coefficients being alternately positive and negative. As anticipated, β is more important than α , and afterwards the convergence is rapid except for the first line.

The Sharp series becomes

$$\nu = 29223.780 - 109679.2/\rho_{m}^{2},$$

$$\rho_{m} = m + 0.7 + \frac{0.018546}{m + 0.7} - \frac{0.077181}{(m + 0.7)^{3}} + \frac{0.02276}{(m + 0.7)^{3}}.$$
(53)

where

The last term is practically negligible even for the line m=3, and the last but one very soon afterwards. But the determination of these coefficients as precisely as possible will ultimately shed light on the nature of spectra.

The formula is not empirical in the ordinary sense, but has been shown to be of the necessary practical form. It is now evident that the values of ρ_m are not simple, and that no formula yet proposed is anything but an empirical approximation.

One remark may be made. It seems probable that the only way to regard the sequence $\rho_1, \rho_2, \ldots, \rho_m$, is as the roots of a transcendental equation, and the probable nature of this equation can be suspected. For the equation

$$\tan x = a + b/x + c/x^2 + \dots \tag{54}$$

has roots which express themselves naturally in this manner. The general behaviour of the coefficients is exactly in accordance with this view.

At the same time, if the Rydberg-Schuster law is true, Rydberg's constant is the same in hydrogen and helium, and vice versa. The law is at the same time certainly true from the earlier part of this paper.

In the Diffuse series, the investigation cannot be pushed so far, for the line m=1 is far in the infra-red and unknown. But Eversheim has measured m=2 (the line D_8) and m=3 accurately enough for our purpose, and m=4 is in the part of the spectrum, near λ 4000, where accurate measurements are possible. But m=5 in this series is known, from the work of Hicks, to be a bad measurement. Our conclusions must, therefore, be drawn from three accurate lines only. Nevertheless they are quite definite, as will appear. The limit of the series is given very accurately by

$$\lambda = 29223.776 + 0.004416 \delta N_{1}$$

and the wave numbers are

$$\nu_2 = 17014.789, \quad \nu_3 = 22357.740, \quad \nu_4 = 24830.479,$$

so that the values of $\rho_m = (109679 \cdot 22 + \delta N)^{\frac{1}{2}}/(A - \nu_m)^{\frac{1}{2}}$ are, on calculation,

$$\rho_{2} = 2.997245 + 0.0^{4}1312 \,\delta N,
\rho_{3} = 3.996769 + 0.0^{4}1696 \,\delta N,
\rho_{4} = 4.996510 + 0.0^{4}2027 \,\delta N.$$
(55)

Since μ is nearly unity in this series, whatever formula be adopted, a Hicks formula, or, in fact, various forms, can give good results. If, for example, we use the Hicks form

$$\rho_m = m + \mu + \alpha/m,$$

then
$$4+2\mu+\alpha=2\rho_1$$
, $9+3\mu+\alpha=3\rho_8$, $16+4\mu+\alpha=4\rho_4$,

whence $2\rho_2 + 4\rho_4 - 6\rho_8 = 2$, and, solving for δN , we obtain

$$\delta N = 15.1. \tag{56}$$

This is already nearer to zero than to Bohr's value.

Now we have every reason to believe that the variable parts of the Diffuse and Sharp series are of the same type. Spectroscopists would hesitate to give up this opinion. If, therefore, we use the Sharp series type with only one constant α , we write

$$\rho_m = m + \mu + \alpha/(m + \mu),$$

and obtain two equations for μ and δN ,

$$\mu = \frac{4\,\rho_4 - 3\,\rho_3 - 7}{2 + \rho_3 - \rho_4} = \frac{3\,\rho_3 - 2\,\rho_2 - 5}{2 + \rho_2 - \rho_3}\,.$$

The results of the arithmetical work are

$$\delta N = -26.4, \quad \mu = 0.99635.$$

The value of δN has passed beyond zero, and when the type of formula found necessary for the Sharp series is employed, the choice lies between zero and a negative value. We cannot add another constant and proceed further, for we lack the line m=1, the line m=5 is inaccurate, and m=6 is too far down to be of use with the present accuracy.

But we can proceed in another way. For in the case of the Sharp series the constant β is as important as α . This may be the case here. If so, a close value of δN can be found by (1) neglecting β as above, and (2) neglecting α , and (3) taking the mean of the two results. For the errors they produce in δN can be shown to be in opposite directions. If, therefore, neglecting α , we write

$$\rho_m = m + \mu + \beta/(m + \mu)^2,$$

and solve the resulting equations, we find, after some reduction,

$$\delta N = +25.2$$

The mean of the two values is $\delta N = \frac{1}{2}(25\cdot2-26\cdot4) = -0\cdot6$, and the true value is evidently again zero. At the same time, $\mu = 0.996704$.

Another calculation has been made, by taking a corrected value for the line m=5 from Hicks' investigation, and using both α and β . The value found for δN was about 3.

The best available value of μ is found by fitting a formula with three constants μ , α , β , to ρ_2 , ρ_3 , ρ_4 , with $\delta N = 0$. The result is

$$\mu = 0.994180$$

but the calculation with m=5 suggests that it is converging to 0.994. It is quite certain that μ is not equal to unity in the Diffuse series.

The more refrangible components of the Diffuse series are given by

$$\nu = 29223.776 - 109679.22/\rho_{\rm m}^2$$

where
$$\rho_m = m + 0.99418 + \frac{0.023438}{m + 0.99418} - \frac{0.074456}{(m + 0.99418)^3}.$$

The Principal Series.

It is perhaps unnecessary to give the complete investigation for the Principal series, which proceeds in the same manner. We again find, though with less accuracy on account of bad measurements, that δN converges closely to zero as the number of constants in the formula increases, and that the only satisfactory form is

$$\rho_m = m + \mu + \alpha/(m + \mu) + \beta/(m + \mu)^2 + ...,$$

which is not very convergent for the first lines.

The leading line is known very accurately, and the next three are fairly reliable, from the results of previous series representations made by Hicks and others. The values of ρ are numerically

$$\rho_1 = 1.937286,$$
 $\rho_2 = 2.933420,$
 $\rho_3 = 3.932255,$
 $\rho_4 = 4.931434.$

The limit is A=38454.943, and the value of μ calculated from the first four lines is $\mu=0.924507$. There is evidence, moreover, of a convergence to 0.925, which further measurements may confirm. Pending such measurements, the only interest of this investigation of the Principal series lies in the fact that N has again Curtis' value.

A consideration of the spectrum of parhelium is left for a later paper.

Summary.

- 1. The limits of series with many lines, for which a Hicks formula is already known, can be calculated with extreme accuracy by a new method.
- 2. The interferometer measures of the leading lines of the helium series enable the best form of the series to be obtained, and this form is an extension of that of Rydberg, dependent on $m + \mu$ and not m.
- 3. The value of Rydberg's constant 109679.2 given by Curtis for hydrogen is the true value for the arc spectrum of helium, and is in fact a rigorous constant for arc spectra. Spark spectra are not treated.
 - 4. The Rydberg-Schuster law of limits is exact for helium.
- 5. It seems probable that μ is a simple fraction whose denominator is a multiple of 5, as Halm has suggested. It is exactly 0.7 for the Sharp series of helium.

The Orbits of a Charged Particle round an Electric and Magnetic Nucleus.

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The following communication is formally a complement to one published in the 'Proceedings' of the Society* on "The Effect of the Magneton on the Scattering of α-Rays."

In the present paper the more general case of a central positively charged nucleus possessing mass and a magnetic moment is considered. The case is treated as if the mass of the nucleus is so large compared with that of the revolving particle that it may be regarded as fixed. It is, therefore, not directly applicable when the revolving body is an α -particle except in cases where the central mass is large compared with that of the hydrogen atom. It is shown later what modification is needed when the motion of the nucleus is not large enough to affect its magnetic quality. The former paper was suggested by certain theories relating to the scattering of α and β -particles by matter. In the present, however, the chief interest lies in the discussion of the nature and properties of the various orbits, more especially of such as do not extend to infinity, or as they may be called "local orbits." In both cases the motion in the equatorial plane of the magneton alone is considered.

Orbits of Positive Particle.

The following specification of the system will be used:-

Charge on the nucleus = ne magnetic = nec static units.

Charge on the moving particle = n'e magnetic = n'ee static units, e being the positive electronic charge and n' = 2 for an α -particle.

Moment of magneton = M.

Mass of moving particle = m.

Suppose the magneton has its N pole above the paper. Then its field will always turn the particle to the left of its path, and, ρ denoting the radius of curvature,

$$\frac{mv^2}{\rho} = (\mathbf{M}n'ev - nn'e^2c^2p)\frac{1}{r^2}.$$

The equation of energy gives

$$\frac{1}{2}mv^2 = \frac{1}{2}mV^2 - \frac{nn'e^2c^2}{r},$$

^{*} Series A, vol. 90, p. 356.

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in which V denotes the velocity at infinity, supposed parallel to the initial line of θ .

These equations may be written

$$\frac{1}{\rho} = \left\{ \frac{a^2}{\sqrt{(1-bu)}} - \frac{\frac{1}{2}pb}{1-bu} \right\} u^3,$$

$$mv^2 = mV^2 (1-bu),$$

$$a^2 = \frac{Mn'e}{mV}, \qquad b = \frac{2nn'e^2c^2}{mV^2}, \qquad u = \frac{1}{x},$$

where

both a and b being of the dimensions of a line.

Since

$$\frac{1}{\rho} = \frac{1}{r} \cdot \frac{dp}{dr} = u^3 \frac{dp}{du},$$

$$\frac{dp}{du} = \frac{1}{2} \frac{b}{1 - bu} p - \frac{a^2}{\sqrt{(1 - bu)}},$$

$$p = \frac{p' - a^2 u}{\sqrt{(1 - bu)}},$$
(1)

whence

where p' is the value of p at infinity.

Apsidal Distances.—These are given by p = r = 1/u, or

$$1 - bu - u^{2}(p' - a^{2}u)^{2} = 0. (2)$$

It will simplify matters if we use a unit of length = a; in other words, write u for au, p for p/a, and b for b/a.

The apsidal distances are then given by the roots of

$$1 - bu - u^2(p' - u)^2 = 0.$$

Tangents to Orbit from O.—When the tangents exist p = 0,

$$u = p'$$
 (or, in ordinary units, $au = p'/a$). (3)

Points of Inflection.—When these exist dp/dr = 0, or ∞ .

This condition gives

$$u=\frac{2-p'b}{b},$$

or, in ordinary units,

$$r = \frac{a^2b}{2a^3 - p'b}. (4)$$

They are, therefore, non-existent if $p' > 2a^2/b$ (in ordinary units), also r > b, therefore $p' > a^2/b$, or points of inflection exist if $p' > a^2/b < 2a^2/b$. Since $p = r^2(d\theta/ds)$, it follows that

$$d\theta = \frac{p'-u}{\sqrt{\{1-bu-u^2(p'-u)^2\}}}du$$

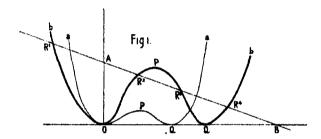
$$= \frac{p'-u}{\sqrt{-\{(u-u)(u-\beta)(u-\gamma)(u-\delta)\}}}du,$$
(5)

where α , β , γ , δ are the roots of the apsidal equation supposed in ascending order of magnitude. It will be shown later that α is always negative.

The apsidal distances are given by the biquadratic

$$1 - bu - u^2 (p' - u)^2 = 0.$$

The roots of this are determined by the intersections of the fixed straight line y = 1 - bu and the curve $y = u^2(p - u)^2$, where now p is written for p'. These vary for given a, b, as p' is changed from $-\infty$ to $+\infty$. The curve is symmetrical with respect to a point at $u = \frac{1}{2}p$, where there is a hump, and has two branches stretching to infinity as in fig. 1, a, b.



If p' is negative, the curve is reversed with respect to OA, whilst the line AB remains unchanged.

As p' increases from 0 to ∞ the curve, while keeping its general shape, grows, the hump at P rising and Q moving out to the right. During this growth the hump may touch the line AB on the inside.

If so, it will again touch for a larger p' on the outside of the line, and between these the hump will cut the line in two points as in fig. 1, b, and the equation has four real roots.

If, on the contrary, the hump does not touch AB as it grows there will never be more than one real positive root. It is clear then that there is always one real negative root and at least one positive, and in certain conditions three real positive ones.

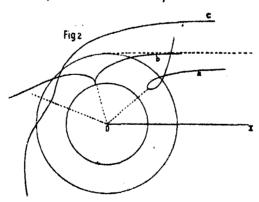
The integration for θ extends from u=0 to the smallest positive root, and in case of three real positive roots, there is another orbit corresponding to integration between the two largest. In other words we get orbits stretching to infinity for all values of p', and, under certain circumstances, orbits always at a finite distance. It is then necessary to determine the criterion for the existence of these "local" orbits.

If p' is negative the curve is reversed relatively to OA and there is always one and only one positive real root. In other words, only orbits extending to infinity can exist. As will be seen immediately, the top of the hump grows

very much more rapidly with increasing u than the ordinate of the line. Consequently, while for p'=0 there will be one negative root only, there is always a value of p' beyond which the hump will cut the line and the equation will have three real negative roots. The negative roots do not of course refer to any actual orbits, but the nature of the reality of the roots will affect the transformation by which the integral giving θ is evaluated.

In fig. 1, Q corresponds to the tangent from the centre to the orbit, the points R to the apses, and B is a point of no velocity.

In the case where (p') being positive) the hump never touches AB, as uincreases from 0 it comes to Q before the apse, so long as OQ is less than OB, i.e. so long as p < 1/b. In this case there are actual tangents from the centre to the orbit, of lengths given by (3). All particles therefore projected from ∞ in lines distant from the nucleus less than a^2/b proceed in orbits with tangents from the centre, and may therefore form loops. When Q is at B, i.e. p = 1/b, the contact points of the tangents and the apse coincide and the velocity is zero. In other words, when the line of projection is at a distance a^2/b cm. from the centre the orbit has a cusp at a distance from the centre As Q advances beyond B, the root lies to the left of B, i.e. u comes to an apse before a possible tangent, and the orbits have no tangents from the centre. On the other hand points of inflection now exist so long as p' < 2/b and when p' = 2/b the point of inflection is at infinity. For p'>2/b they do not exist. In fig. 2, a, b, c illustrate the nature of these orbits when nearest the nucleus. The figure is only diagrammatic. The inner circle has radius b, the outer radius a^2/b .



In the case here considered there can be no combined atomic system.

In the second case the hump may cut the line AB in two points. Suppose it first touches it for a value of $p' = p_1$, and touches it outside for the value $p' = p_2$. For $p' = p_1$ the orbits are similar to those in the case just considered

with tangents from O, that is, in general, loops. But as p' becomes nearly equal to p_1 we have the roots β and γ of equation (5) becoming equal, and θ becoming very large as u approaches the neighbourhood of β . In other words as the particle approaches from infinity and gets within a distance α/β it makes a large number of almost circular revolutions and then again unravels itself until it reaches an apse by means of a loop. When $p'=p_1$ the single orbit becomes two-one from infinity ultimately revolving in a circle of radius a/β and unravelling itself after an infinite time by a corresponding path to infinity; the other with one loop, having tangents from the centre approaching asymptotically from the inside to the same circle. It clearly corresponds to a circular orbit with instability. When p' lies between p_1 and p_2 there are two branches—one due to integration from u=0 to $u=\beta$ and the second from $u = \gamma$ to $u = \delta$. The first is from infinity, has no tangent from O, and a single apse α/β . The second is a local orbit with apsidal distances a/γ and a/δ . As p' increases from p_1 to p_2 , Q moves out to B and then beyond. In other words, for $p' < a^2/b$ Q lies between the apses, and there are tangents from O, i.e. scrolls with loops. When Q is at B the loops degenerate to cusps. For larger values of p' up to p_2 , Q is outside B, there are no tangents, but, as before, points of inflection occur. As p' approaches p_2 the roots γ , δ , tend to equality, θ becomes very large. That is the orbit again becomes a circle when $p' = p_2$ with a radius a/δ . This radius is greater than the cuspidal case and less than the unstable circular orbit above. It is therefore stable, i.e. a slight disturbance does not send the particle to infinity.

It is clearly important to know the conditions which discriminate between these two cases. To do this it is necessary as a preliminary to discuss some points as to the nature of the hump.

The equation to the curve is

$$y = u^2 (p-u)^2.$$

The peak of the hump is given by

$$u = \frac{1}{2}p, \quad y = p^4/16,$$

and its locus therefore is $y = u^4$, i.e. the same as the curve for p = 0.

$$dy/du = 2u(p-u)(p-2u).$$

There are points of inflection given by

$$p^{3} - 6pu + 6u^{2} = 0,$$

$$u = \frac{1}{2}p(1 \pm 1/\sqrt{3}).$$
(6)

whence

For the point farthest out

$$u = \frac{1}{2}p(1+1/\sqrt{3}).$$

At the point of inflection

$$\frac{dy}{du} = -\frac{p^3}{3\sqrt{3}},$$

$$y = \frac{p^4}{36} = \frac{4}{9} \times \text{height of the peak}.$$

If p' be increased from a given value

$$dy/dp = 2u^2(p-u) = +$$
 so long as $u < p$.

That is, if p be increased, the hump of the new curve lies wholly outside the old one.

Discrimination of Cases i and ii.—It is clear that if the inclination of the tangent at the point of inflection is $\langle \tan^{-1}b \rangle$, the curve can never cut the line AB in more than two points. Consider the case where the point of inflection lies on the line and touches it, that is, choose p' so that the point of inflection is on it, and then b, so that the corresponding dy/du = -b.

p' is given by

$$p^{4}/36 = 1 - \frac{1}{2}bp(1 + 1/\sqrt{3}),$$
$$-b = -v^{3}/3\sqrt{3}.$$

also

Eliminating p, the condition for the possibility is

$$b = \{4(2-\sqrt{3})/\sqrt{3}\}^{\frac{1}{2}},$$

or, using ordinary units,

$$b = \{4(2-\sqrt{3})/\sqrt{3}\}^{\frac{1}{4}}a = 0.6976921...a,$$

and then

$$p'/a = \{4(2-\sqrt{3})/\sqrt{3}\}^{\frac{1}{2}}\sqrt{3} = 1.536202...$$

Suppose p', b/a, have the above values. Then, with p' greater, dy/du at the point of inflection increases. With p' less, the hump cannot cut the line in two points, and with p' greater, the humps always lie outside the above critical one, and therefore will not cut in more than one point. If, however, the tangent at the point of inflection when it is on the line is $> \tan^{-1}b$, it will cut in two points. Hence the discrimination is that for two points on the hump (or four roots in all), dy/du of the point of inflection when on the line must be numerically >b. In other words—

for Case i
$$b > 0.6976921 \dots a.$$
 (7)

In case ii, with b/a < 0.697..., the apsidal equation will have four real roots for values of p' between two limiting values p_1 , p_2 , corresponding to the two cases when the hump touches the line (a) below AB and (b) above.

In other words, p_1 , p_2 , must be such as to make the apsidal equation have equal roots. Consequently

$$1 - bu - u^{2}(p-u)^{2} = 0$$

-b-2u(p-u)(p-2u) = 0.

The equation for the p values, found by the elimination of u, is found to be

$$4bp^5 - 4p^4 + b^3p^3 + 30b^2p^2 - 9bp + 64 + 27b^4/4 = 0,$$
 (8)

and the course of the elimination gives for the corresponding double roots of the apsidal equation

$$u = \frac{24b - 3b^2p - 4p^3}{18b^2 - 8p^3 + 4bp^3} \tag{9}$$

in which p is a root of the above quintic.

Since the sum of the four roots of the apsidal equation is 2p and their product -1, the sum of the other two is 2(p-u) and their product $-1/u^2$, where u is the double root (9). Hence the other two roots are

$$p - u \pm \sqrt{(p - u)^2 + 1/a^2}.$$
 (10)

The diagrams show that there will always be one negative root of (8) (as is clear from the equation itself) and two real positive roots if b/a < 0.697..., and no more.

The Angular Co-ordinate in the Orbit.—Equation (5) gives

$$\theta = \int_0^u \frac{(p'-u) du}{\sqrt{-\left\{(u-\alpha)(u-\beta)(u-\gamma)(u-\delta)\right\}}} = \int_0^u \frac{p'-u}{\sqrt{-Y}} du \quad \text{(say)}$$

for the infinite branch, with apsidal angle given by the upper limit $u = \beta$. When a local orbit exists, i.e. γ , δ , real

$$\theta = \int_{-\infty}^{u} \frac{p' - u}{\sqrt{-Y}} du,$$

with apsidal angle given by the upper limit $u = \delta$ and the tangential angle by u = p (when $p < \delta$).

In a particular case, the first step is to solve the apsidal equation, and then apply a transformation by the known methods to reduce the elliptic integral to a canonical form. As the chief interest of the present communication is in connection with local orbits, i.e. orbits lying wholly within a finite distance of the centre, it will be necessary only to carry out this work for the case where all the roots are real, and p' positive. For the infinite branches $u > 0 < \beta$, using the quadric transformation, write*

$$u = \frac{\alpha(\delta - \beta) + \delta(\beta - \alpha)\sin^2\phi}{\delta - \beta + (\beta - \alpha)\sin^2\phi},$$

^{*} Notation and formulæ of Briot and Bouquet, 'Théorie des Fonctions Elliptiques,' p. 428.

$$k^{2} = \frac{(\beta - \alpha)(\delta - \gamma)}{(\gamma - \alpha)(\delta - \beta)}$$
 (anharmonic ratio of R₁, R₂, R₃, R₄ in fig. 1),

whence

$$\sin^2 \phi = \frac{(\delta - \beta)(u - \alpha)}{(\beta - \alpha)(\delta - u)}$$
 (inverse ratio of R₁, R₂, P, R₄).

When
$$u = 0$$
, $\sin \phi = \sqrt{-\frac{\alpha}{\delta} \left(\frac{\delta - \beta}{\beta - \alpha}\right)} = \sin \phi_0$ (say)
 $u = \beta$, $\phi = \pi/2$.

Also from the apsidal equation

$$p' = \frac{1}{6} (\alpha + \beta + \gamma + \delta)$$

Making the substitutions

$$\theta = \frac{\alpha + \beta + \gamma - \delta}{\sqrt{(\gamma - \alpha)(\delta - \beta)}} \int_{\phi_{a}}^{\phi} \frac{d\phi}{\sqrt{(1 - k^{2} \sin^{2} \phi)}} + 2 \frac{(\delta - \alpha)(\delta - \beta)}{(\beta - \alpha)\sqrt{(\gamma - \alpha)(\delta - \beta)}} \int_{\phi_{0}}^{\phi} \frac{d\phi}{(n + \sin^{2} \phi)\sqrt{(1 - k^{2} \sin^{2} \phi)}}$$
where
$$n = \frac{\delta - \beta}{\beta - \alpha}, \quad \sin \phi_{0} = \sqrt{-\frac{n\alpha}{\delta}}.$$
(11)

The apsidal angle Θ is given by $\phi = \pi/2$, or

$$\Theta = \frac{\alpha + \beta + \gamma - \delta}{\sqrt{(\gamma - \alpha)(\delta - \beta)}} \left\{ F(\pi/2) - F(\phi_0) \right\} + 2 \frac{(\delta - \alpha)(\delta - \beta)}{(\beta - \alpha)\sqrt{(\gamma - \alpha)(\delta - \beta)}} \left\{ \Pi(\pi/2) - \Pi(\phi_0) \right\}.$$

In the cuspidal case, where p = b, $\alpha + \beta + \gamma - \delta = 0$, and the first elliptic integral F does not enter.

For the local orbits the integration is from $u = \gamma$ up to $u = \delta$, k has the same value as above, but the transformations are given by

$$u = \frac{\gamma(\delta - \beta) - \beta(\delta - \gamma)\sin^2\phi}{\delta - \beta - (\delta - \gamma)\sin^2\phi}, \qquad \sin^2\phi = \frac{(\delta - \beta)(u - \gamma)}{(\delta - \gamma)(u - \beta)},$$

with $\phi = 0$ when $u = \gamma$, and $\phi = \pi/2$ when $u = \delta$,

$$\theta = \frac{\alpha - \beta + \gamma + \delta}{\sqrt{(\gamma - \alpha)(\delta - \beta)}} F(\phi) + 2 \frac{(\gamma - \beta)(\delta - \beta)}{(\delta - \gamma)\sqrt{(\gamma - \alpha)(\delta - \beta)}} \Pi(\phi), \quad (12)$$

where now

$$n = -\frac{\delta - \beta}{\delta - \gamma},$$

and the apsidal angle is given by $\phi = \pi/2$.

For the cuspidal case, the largest root is given by $\delta = 1/b$, and the others, therefore, by the cubic

$$bu^3 - u^2 + b^2 = 0.$$

To solve this, put $u = \frac{1}{2}b\sqrt{3}\sec\phi$, then

$$\cos 3\phi = -\frac{3\sqrt{3}}{2}b^2 = -\cos 3\chi$$

where $3\chi < \pi/2$.

Then

$$\phi = 2n\frac{\pi}{3} \pm \left(\frac{\pi}{3} - \chi\right)$$

and the roots are

$$\alpha = \frac{b\sqrt{3}}{2}\sec(\pi - \chi) = -\frac{b\sqrt{3}}{2}\sec\chi,$$

$$\beta = \frac{b\sqrt{3}}{2}\sec(\pi/3 - \chi),$$

$$\gamma = \frac{b\sqrt{3}}{2}\sec(\pi/3 + \chi),$$

$$\delta = \frac{1}{7} = \frac{3b\sqrt{3}}{3}\sec^3\chi.$$

with

For real roots, therefore, $b < \sqrt{\frac{2}{3\sqrt{3}}} < 0.62$. This is less than the general

limit for four real roots, as it clearly should be. If b is larger, χ is a pure imaginary = $\chi'i$, where $\cosh 3\chi' = 3\sqrt{3b^2/2}$, and we have the roots

$$\alpha = -\frac{b\sqrt{3}}{2^{-}} / \cosh \chi' \qquad \text{(real)}$$

$$\begin{vmatrix} \beta \\ \gamma \end{vmatrix} = \frac{b\sqrt{3}}{4} \frac{\sqrt{3}\cosh \chi' \pm i \sinh \chi'}{\cos^{2}(\pi/3) - \cosh^{2}\chi'}.$$

The above give for all roots real

$$k^{2} = \frac{\cos(\pi/6 - \chi)\cos^{3}(\pi/3 + \chi)}{\cos(\pi/6 + \chi)\cos^{3}(\pi/3 - \chi)},$$

$$n = \frac{4}{\sqrt{3}} \frac{\cos^{3}(\pi/3 - \chi)\cos\chi}{\cos(\pi/6 + \chi)\cos3\chi} \text{ for the infinite branch,}$$

$$n = -\frac{\cos^{2}(\pi/3 - \chi)}{\cos^{2}(\pi/3 + \chi)} \text{ for local orbit,}$$

whilst the equation for the local orbit is

$$\theta = \sqrt{\frac{2\cot(\pi/3 - \chi)}{\cos \pi/6}} F(\phi) + \frac{\sin 2\chi}{\cos^2(\pi/3 + \chi)} \sqrt{\{2\cos(\pi/6)\cot(\pi/3 - \chi)\}} \Pi(\phi).$$

The limiting cases, however, i.e. corresponding to equal roots of the apsidal equation, do not require elliptic functions. The first corresponds to $\beta = \gamma$ and belongs to an orbit from infinity, the other to $\gamma = \delta$ and belongs to a local circular orbit. In the first

$$\theta = \int_0^u \frac{p-u}{(\beta-u)\sqrt{(u-a)(\delta-u)}} du,$$

whence, remembering that $p = \frac{1}{2}(\alpha + 2\beta + \delta)$,

$$\theta = \sin^{-1} \frac{\alpha + \delta}{\delta - \alpha} - \sin^{-1} \frac{\delta + \alpha - 2u}{\delta - \alpha} + \frac{1}{2} \frac{\delta + \alpha}{\sqrt{(\beta - \alpha)(\delta - \beta)}} \times \log_{\epsilon} \frac{\beta}{\beta - u} \frac{\beta(\delta + \alpha)/2 - \alpha\delta - [\beta - (\delta + \alpha)/2]u + \sqrt{(\beta - \alpha)(\delta - \beta)(u - \alpha)(\delta - u)}}{\beta(\delta + \alpha)/2 - \alpha\delta + \sqrt{-\alpha\delta(\beta - \alpha)(\delta - \beta)}},$$
(13)

and for the local orbit, integrating from u to δ ,

$$\theta = -\frac{1}{2}\pi + \sin^{-1}\frac{2u - \alpha - \delta}{\delta - \alpha} + \frac{1}{2}\frac{\delta + \alpha}{\sqrt{(\beta - \alpha)(\delta - \beta)}}$$

$$\times \log_{e}\frac{\delta - \beta}{u - \beta}\frac{\beta(\delta + \alpha)/2 - \alpha\delta - [\beta - (\delta + \alpha)/2]u + \sqrt{(\beta - \alpha)(\delta - \beta)(u - \alpha)(\delta - u)}}{\frac{1}{2}(\delta + \alpha)(\delta + \beta) - \delta(\beta + \alpha)}.$$
(14)

In the latter the angular co-ordinate is measured from the apse $u = \delta$. In both, of course, the apsidal angle is infinite.

In the particular case of three equal roots, where $b = \left\{4\frac{2-\sqrt{3}}{\sqrt{3}}\right\}^{\frac{1}{4}}$, the orbit from infinity becomes

$$\theta = \frac{\delta + \alpha}{\delta - \alpha} \left\{ \sqrt{\frac{u - \alpha}{\delta - u}} - \sqrt{-\frac{\alpha}{\delta}} \right\} + \sin^{-1} \frac{\delta + \alpha}{\delta - \alpha} - \sin^{-1} \frac{\delta + \alpha - 2u}{\delta - \alpha},$$

whilst the local orbit merges in the asymptotic circle $u = \delta$, or r = 0.8254a. In the above δ is the abscissa of the point of inflection on the hump, i.e. $\delta = \frac{1}{2}p(1+1/\sqrt{3}) = \frac{1}{2}(\sqrt{3}+1)b^{\frac{1}{2}}$. The sum of all the roots of the apsidal equation is 2p. Hence

$$\alpha = 2p - 3\delta = -\frac{\sqrt{3}}{2}(\sqrt{3} - 1)b^{\frac{1}{2}}$$

Substituting these values, the equation to this orbit becomes

$$\theta = \frac{\sqrt{3-1}}{2} \left\{ \sqrt{\frac{u + \frac{1}{2}\sqrt{3}(\sqrt{3-1})b^{\frac{1}{2}}}{\frac{1}{2}(\sqrt{3+1})b^{\frac{1}{2}} - u}} - (\sqrt{3-1})\sqrt{\frac{\sqrt{3}}{2}} \right\} + \sin^{-1}\frac{2u - (\sqrt{3-1})b^{\frac{1}{2}}}{2b^{\frac{1}{2}}} + 21^{\circ}28',$$

or putting in numerical values, and returning to ordinary units

$$\theta = \left\{0.1165 \sqrt{\frac{\alpha u + 0.5623}{1.2115 - \alpha u}} + 0.0400\right\} \pi + \sin^{-1}(1.1275 \alpha u - 0.3660).$$

It is interesting to note that this orbit is in plan altogether independent of the constitution of the nucleus—i.e. of M, n, n, e. Its size alone depends on it. With a given constitution, the definite value of b/a required determines the energy of the system—which then gives the value of a (see below).

The foregoing may be illustrated by a numerical example. In order

that local orbits may be possible it is necessary, as we have seen, that b/a < 0.6976... Let us take then b/a = 0.5.

The apsidal equation is then

$$1 - \frac{1}{2}u - u^2(p - u)^2 = 0.$$

The limiting values of p for these orbits are the two positive roots of

$$2p^5-4p^4+\frac{1}{5}p^3+\frac{15}{5}p^2-48p+64\frac{27}{5}=0.$$

They are p = 1.7067, 2.0324.

The apsidal equation gives the following roots:-

For p	== 1.7067.	For 3	o=2.0324.
a = -	 0· 50 59	a ==	-0.4462
$\beta =$	1.0330	$\beta =$	0.5802
$\gamma =$	1·033 0	γ =	1.9654
δ =	1.8530	δ =	1.9654

The orbits for p = 1.7067 are—for the path from infinity

$$\theta = 0.5995 \log_{\epsilon} \frac{1.0330}{1.0330 - u} \cdot \frac{1.4538 - 0.3199 u + \sqrt{(u + 0.5059)(1.8530 - u)}}{2.4220}$$

$$+\sin^{-1}\frac{u-0.6735}{1.1794}+0.5709$$

and for the local orbit, the same expression with

$$\frac{0.8197}{u-1.0330}$$
 in place of $\frac{1.0330}{1.0330-u}$

in which in ordinary units u = a/r; for p = 2.0324, the local orbit is a circle $r = a/\delta = 0.5084a$.

For the cuspidal orbit p=2 and the roots of the apsidal equation are $\alpha = -0.4516$, $\beta = 0.5970$, $\gamma = 1.8546$, $\delta = 2$.

The equations for the orbits are then

(a) Orbit to infinity—

$$\theta = 3.6471 \{\Pi(n, k, \phi) - \Pi(n, k, \phi_0)\},$$

with

$$k^9 = 0.04712$$
, $n = 1.3380$, $\phi_0 = 33^{\circ} 20'$,

(b) Local orbit—

$$\theta = 1.5600 \,\mathrm{F}(\phi) + 13.492 \,\mathrm{\Pi}(n, k, \phi),$$

with

$$k^2 = 0.04712, \qquad n = -9.6494.$$

The apsidal angles are respectively

$$\Theta = 102^{\circ} 43'$$
, $7^{\circ} 25'$

The angle between two successive cusps in the local orbits is therefore 14° 50′.

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With the same value of b we may take p=1.85—about midway between the two limits—for an example of looped orbits. For this value of b, however, the cusped orbit is so close to the inner limit that the inflexional orbits cover a very small region. With p=1.85, the apsidal roots are $\alpha=0.4782$, $\beta=0.7016$, $\gamma=1.5358$, $\delta=1.9408$. The equation to the local orbit is

$$\theta = 1.454 \,\mathrm{F}(\phi) + 3.231 \,\mathrm{\Pi}(n, k, \phi),$$

with
$$k^2 = 0.1914$$
, $n = -3.060$, $\sin^2 \phi = 3.060 \frac{u - 1.5358}{u - 0.7016}$.

The apsidal angle is 15° 11' and the tangent from the centre makes an angle 2° 53' with the line to the inner apse. The apsidal distances are 0.651a and 0.513a and the length of the tangent, 0.540a.

In this case the force due to the magnetic field is to the right of the path, and the electric force is attractive. Hence, with the same notation as before,

$$mv^2/\rho = (-\operatorname{Mev} + nn'e^2c^2p)u^3,$$

$$\frac{1}{2}mv^2 = C + nn'e^2c^2/r,$$

in which, however, C will be negative for cases where the energy is less than that due to a fall from infinity. Write $C = \frac{1}{2}mV^2f$ where f = +1 for paths from infinity and f = -1 when the energy is less than that from infinity.

Then as before it may be shown that

$$p = \frac{p' + a^2 u}{\sqrt{(bu + f)}}.$$

The apses are given by the biquadratic

$$f + bu - u^2(p' + a^2u)^2 = 0$$
;

or, taking the unit of length = a, by

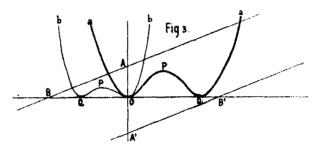
$$f + bu - u^2(p+u)^2 = 0.$$

Case i.—Energy greater than that from Infinity, or f = +1.—The roots are given by the intersections of y = 1 + bu and $y = u^2(p+u)^2$.

Fig. 3b corresponds to p' positive. There is always one, and only one positive root—the largest root δ . In other words there is always an infinite branch with one apse, and no tangent from the centre, for Q lies to the left of O.

Fig. 3a corresponds to p' negative. There is always one real positive root, and may be two more if the hump can cut the line. Since the locus of the top of the hump is $y = u^4$ it must cut y = 1 + bu somewhere, since its ordinate increases with u much faster than that of the line.

There will thus be local orbits for values of p' greater than some critical value, viz., for the case of two equal roots. This corresponds to the case



of the positive particle, in which the infinite orbit and the local orbit have a common asymptotic circle. The conditions for this case can be written down at once from the equations for the case of the positive particle already obtained by writing -b for b and -p' for p'.

Thus the points of inflection are from equation (4) given by

$$u = p' - 2/b,$$

and exist so long as p' > 2/b, or $p' > 2a^2/b$ in ordinary units.

There are therefore none with p' negative.

The conditions for four real roots of the apsidal equation, i.e. for a local orbit, are found from equation (8) to be the negative root of the unaltered equation, viz.,

$$4bp^{6}-4p^{4}+b^{3}p^{3}+30b^{2}p^{2}-96bp+64+27b^{4}/4=0.$$

The angular co-ordinate θ is given by

$$\theta = \int \sqrt{-\{(u-\alpha)\frac{(u+p')\,du}{(u-\beta)(u-\gamma)(u-\delta)\}}}\,$$

in which it is to be remembered that p' is essentially negative. For the infinite branch the integration extends from u = 0 up to $u = \beta$, and for the local orbit from $u = \gamma$ to $u = \delta$. The orbit $\beta = \gamma$ is expressible in logarithmic functions, with asymptotic circles, but there is none corresponding to $\gamma = \delta$. Further, in this motion, contrary to that of the positive particle, u may have infinitely great values—that is, local orbits exist in which the revolving particle may be as close as desired to the centre even with a velocity greater than that due to a fall from infinity—supposed, of course, that it does not come close enough to interfere with the structure of the magneton or the nucleus. The existence of these combinations with extreme energy has its clear suggestions in connection with the theory of the inner electrons of atomic theory. They cannot exist with electric attractions only. Naturally, also, if the velocities are comparable with that of light the whole theory is inapplicable.

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The signs of the p' in local orbits refer to directions of motion round the centre.

In this case i, the transformations to reduce the elliptic integrals to the canonical form are the same as in the former case.

Case ii.—Energy less than that from Infinity, or f = -1.—The apsidal equation is

$$-1 + bu - u^2(p' + a^2u)^2 = 0.$$

In this case, in the diagram of fig. 3 the line is displaced to A'B', and the curve (b) corresponds to p' positive. There is clearly no real root, or two only. The limit for the two is found by the condition that the curve touches the line, which gives a critical value for p'. Since dy/dp for the curve is positive for u positive the curve grows steeper with increasing p. Hence for two real roots p' must be less than this critical value. If the apsidal equation be written

$$1 - bu + u^2 (p' + a^2 u)^2 = 0,$$

it can be transformed from the former equation by writing -p'i for p' and a^2i for a^2 . If the equation for the critical p be thus transformed from equation (8) the corresponding equation for this case becomes

$$4bp^{5} + 4p^{4} - b^{3}p^{8} + 30b^{2}p^{2} + 96bp + 64 - 27b^{4}/4 = 0.$$
 (15)

with the corresponding

or

or

$$u = \frac{24b + 3b^2p - 4p^3}{18b^2 + 8p^2 + 4bp^3}.$$

In order, then, to have orbits with p' positive, i.e. rotating anti-clockwise, it is necessary for the above equation to have a positive root. It is clear from fig. 3b that there cannot be more than one. Hence p = 0 and $p = \infty$ must make the expression change sign, and this it cannot do unless $64 - 27b^4/4$ is negative. Hence the required condition is

$$27b^4/4 > 64,$$

 $b>4/3^2>1.754766...,$

with $b = 4/3^2$, p = 0, and the two equal roots of the apsidal equation are

$$u = 4/3b = 3^{-\frac{1}{4}}$$

 $r = 3^{\frac{1}{4}}a$ in ordinary units.
 $= 1.316074...a$.

This gives a circular orbit. When b is greater than the above the equation (15) has one real positive root, say p_1 . Then for any value of p' less than this, there results a local orbit with two apsidal distances, and no

tangent from the centre. The orbit, in fact, encloses the nucleus without any loops.

Fig. 3a corresponds to p' negative, or a clockwise direction of motion. Here clearly there may be no real positive roots, or two or four, to the apsidal equation. As -p' increases, the right-hand branch of the curve must cut the line for some value of -p' greater than the largest root of equation (15), which equation always has at least one real negative root. It does not necessarily follow that it has three real ones—or that the apsidal equation has four real positive roots—unless b satisfies some condition. This condition is determined in a similar way to the corresponding case for the positive particle. The line must be steeper than a certain amount, i.e. b > a critical value. This is determined by the condition that the point of inflection must lie on the line and the line touches the curve there. But here it is necessary to take the point of inflection which is nearer to the The condition is then found to be that

$$b > \left(4\frac{2+\sqrt{3}}{\sqrt{3}}\right)^{2} > 5.030195...$$

which may be compared with the corresponding value in the former case

$$b < \left(4\frac{2-\sqrt{3}}{\sqrt{3}}\right)^{3} < 0.697...$$

The cases of all roots imaginary occur when the line does not cut the curve of p' = 0. The condition of this has been found for p' positive above. If $b > 4 \times 3^{-4}$ there will always be at least two roots.

The figure shows that with some particular value of p, viz. -1/b, Q will fall on B. For p' less than this value there are no tangents to the orbit. For p' = -1/b there will be cusps for the smaller of the u-roots, i.e. the cusps point outwards. For -p' > 1/b, Q lies between the two largest roots, tangents from O exist, and the orbit has loops. When there are four roots, the orbit with the largest roots has tangents from O, the other not: that is the inner orbit has loops, the outer not.

Points of inflection are given by

$$u = 2/b - p' = 2OB - OQ.$$

When therefore Q is on the right of B, u < OB, and as u is always greater than OB points of inflection do not exist. That is orbits with cusps or loops have no points of inflection. When Q is on the left of B, u > OB, and it is not impossible for such to exist. To determine whether they actually exist it is necessary to find whether the value of u lies between the roots γ , δ , or α , β : i.e. whether the value of $-1 + bu - u^2(p-u)^2$ is positive when 2/b-p is inserted for u, and p' < 1/b = 1/b-x (say). It becomes

or

 $bx-(1/b+x)^2x^2=x\{b-x(1/b+x)\}$. When u is small this is +. That is the orbits near the cuspidal ones have points of inflection, and they will exist so long as $2/b-p'>\gamma$.

Effect of Inertia of the Nucleus.—In the foregoing the nucleus has been treated as fixed. This will introduce no appreciable error in the case where the revolving particle is an electron. The error, however, may be considerable for a revolving particles, even when the mass of the nucleus itself is large, and the theory is inapplicable as it stands to systems comparable with H or He atoms. Throughout the assumption is made that the velocities are small compared with that of light, and that energy losses due to accelerations are negligible. Under these circumstances the electric forces on the nucleus and its satellite are equal and opposite, and so far as they are concerned the common centre of gravity may be regarded as fixed. The case of the magnetic forces, however, is not so clear. That there is a resultant reaction equal to the magnetic force on the moving particle we naturally assume with Newton's third law; but it does not follow that this reaction is concentrated on the magneton, and that there is nothing on the medium itself or its boundary. The following considerations, however, show that for the problem under consideration, the reaction on the nucleus is equal and opposite to that on the moving particle—viz.: Mev/r^3 along the normal. The moving particle produces a magnetic field in circles round its direction of motion. Let H denote this force at O and let ON be the perpen-Then (decomposing M into its dicular from O on the line of motion. elements m, -m, at distance l) it is easy to show that the force on the magneton is along ON and is MH/ON. But if v^2/c^2 is negligible $H = evON/r^3$. Hence the force is Mev/r^3 , the same in magnitude as that on the moving particle. To this extent, therefore, we may be justified in regarding the centre of gravity as fixed. We make also another supposition that the motion of the magneton does not affect its properties.

If r denote the distance of the moving particle from the centre of gravity, the distance from the nucleus is (1+m/m')r = kr(say). The forces along the normal are, therefore, $Mn'ev/k^3r^3$ due to the magneton, and $nn'e^2c^2p/k^3r^3$ due to the component of the electric force. Also the energy equation gives

$$\begin{split} k\,\tfrac{1}{2}\,mv^2 &= k\,\tfrac{1}{2}\,m\mathbf{V}^2 - \frac{nn'e^2e^2}{kr}\,,\\ \\ \tfrac{1}{2}\,mv^2 &= \tfrac{1}{2}\,m\mathbf{V}^2 - \frac{nn'e^2e^2}{k^2r}\,. \end{split}$$

The theory is therefore precisely similar to that developed above, in which a^2 is replaced by a^2/k^3 and b by b/k^2 .

Circumstances of Projection.—These give the velocity of projection, the distance from the nucleus, and the angle the direction of projection makes with this. The velocity gives, with distance, the energy $\frac{1}{2}mV^2$ of the system. From this a^2 and b can be calculated.

If u' be the inverse distance, p the perpendicular, and ϕ the direction of motion, $pu' = \cos \phi$. The corresponding value of p' is then found from equation (1), viz.:—

$$p' = a^2u' + \frac{\sqrt{(1-bu')}}{u'}\cos\phi.$$

The actual orbit is then determined by the methods already developed.

Numerical Values.—Let E denote the total energy of the system, i.e. the kinetic energy when the potential is zero, or in case of energy less than from infinity, the potential energy when the kinetic is zero. The quantities now determining the orbits are the two:—

$$a^2 = \frac{\mathbf{M}n'c}{\sqrt{(2m)\sqrt{\mathbf{E}}}}, \qquad b = \frac{nn'c^2c^2}{\mathbf{E}}.$$

We shall regard M as consisting of a whole number N of magnetons and take

$$M = 1.6 \times 10^{-21} \text{ N}.$$

$$e = 1.55 \times 10^{-20}.$$

$$ee = 4.65 \times 10^{-10}.$$

$$m \text{ for H} = 1.6 \times 10^{-24}.$$

$$m \text{ for electron} = 0.84 \times 10^{-27}.$$

Energy of α -particle moving with velocity of light = 2.88×10^{-3} .

Energy of mass of electron moving with velocity of light = 3.78×10^{-7} .

Further it will be convenient to measure $\mathbf E$ above, as a fraction x of these quantities, so that

For
$$\alpha$$
-particle $E = 2.88 \times 10^{-3} x$.
For electron $E = 3.78 \times 10^{-7} x$.

With these values we get-

(i) For
$$\alpha$$
-particles—
$$a^2 = 1.29 \,\mathrm{N}n'x^{-\frac{1}{2}}10^{-28}. \qquad a = 1.13 \,\mathrm{N}^{\frac{1}{2}}n'^{\frac{1}{2}}x^{-\frac{1}{2}}10^{-14}.$$

$$b = 7.50 \,nn'x^{-\frac{1}{2}}10^{-17}. \qquad b/\alpha = 6.63 \,\mathrm{N}^{-\frac{1}{2}}nn'^{\frac{1}{2}}x^{-\frac{1}{2}}10^{-2}.$$

The volume a^4/b is independent of the energy. It corresponds to that of a sphere of radius $3.75 \, (N^2n'/n)^3 10^{-14}$.

(ii) For electron—

$$a^{2} = 0.98 \,\mathrm{N}n'x^{-\frac{1}{2}}10^{-24}, \qquad a = 0.99 \,\mathrm{N}^{\frac{1}{2}}n'^{\frac{1}{2}}x^{-\frac{1}{2}}10^{-12},$$

$$b = 5.72 \,nn'x^{-1}10^{-13},$$

$$a^{2}/b = 1.73 \,\mathrm{N}n^{-1}x^{\frac{1}{2}}10^{-12}, \qquad b/a = 0.577 \,\mathrm{N}^{-\frac{1}{2}}nn'^{\frac{1}{2}}x^{-\frac{1}{2}},$$

whilst the radius of the sphere corresponding to a^4/b is $7.43(N^2n'/n)^{\frac{1}{2}}10^{-13}$.

In order that combined atoms consisting of one α -particle (n'=2) may exist, b/a < 0.697—whence

$$x > 0.0032 (n^2/N)!$$

corresponding to a velocity when free $>0.056 (n^2/N)^{\frac{1}{2}}c$; or the sizes of possible orbits are of the order of $a^2/b > (N^2/n)^{\frac{1}{2}}10^{-13}$.

The cusped orbit for the limiting case above—i.e. the nearest in—is $b=0.47 \, (N^2/n)^{\frac{1}{2}} 10^{-13}$. We should expect the velocity of the α -ray, when expelled, to be about $(n^2/N)^{\frac{1}{2}}/20$ of light. That of Ra is about one-twentieth. All that can be expected from the present theory is information as to the order of effects—dealing as it does with one revolving particle only. It is interesting, therefore, to find that the orbits which correspond to radioactive instability (asymptotic circles) give values of velocity of emission comparable with those observed.

In case of revolving electrons there are two types. First, that in which the energy is less than that from infinity, in which, therefore, a combined atom may be regarded as of a more permanent type, secondly, that in which the atom retains in combination the electron, even though the energy be greater than that from infinity—the β -radiation analogue. The condition for the latter type is b/a > 5.030. This gives

$$x < 0.0557 (n^2/N)^{\frac{1}{3}}$$
, Free velocity $< 0.236 (n^2/N)^{\frac{1}{3}}c$, $a^2/b < 4.06 (N^2/n)^{\frac{1}{3}}10^{-13}$, $b > 1.0 (N^2/n)^{\frac{1}{3}}10^{-11}$.

[Note, March 20.—By a reference given by Dr. Allen my attention has been drawn to the fact that the problem of the motion of an electron round a magneton and electric charge has already been considered in its most general aspect by Störmer. I have not been able to see the original paper of the latter ('Christiania Forhandl.,' 1907), but he has given a résumé of his results in the 'Comptes Rendus' (see especially vol. 156 (1913), pp. 450, 536). The generality of his method, however, would not appear to be susceptible of easily giving a detailed discussion of the orbits themselves and does not cover the ground of the present paper.]

The Elastic Properties of Steel at Moderately High Temperatures.

By F. E. Rowert, B.A. (Whitworth Scholar), Research Student in the University of Cambridge.

(Communicated by Prof. B. Hopkinson, F.R.S. Received February 6, 1915.)

In a recent paper the author gave the results of measurements of the elastic hysteresis of steel tubes, when subjected to torsional stress, within what is ordinarily regarded as the elastic limit. Those measurements were made at ordinary room temperature, and the chief points established by them were, that the hysteresis of the hard-drawn tubes is much less than that for the same tubes after annealing, and that in the latter case, the loss of energy in the cycle of stress is independent of the speed of performance of the cycle, or, in other words, time is not a factor in the stress-strain relation.

The present research is the outcome of a suggestion by Prof. B. Hopkinson, that at a suitable temperature the hard-drawn tube, which contains a good deal of amorphous material, would begin to behave like a viscous fluid, that is, it would flow more or less freely when under stress, whereas at the same temperature, the annealed tube, being crystalline, though it might take a permanent set, could not flow, or would flow in a much less degree corresponding to the small amount of amorphous material in it.

These predictions have been verified. At a temperature about 300° C., the hard unannealed tube began to show properties similar to those of pitch at ordinary temperatures, or of glass at a temperature rather below the softening point. It is still highly elastic under rapidly varying stress, but flows perceptibly when the stress is applied for a long time. The energy dissipated in a cycle of stress now depends on the speed of the cycle. If the cycle is performed in 5 seconds the area of the closed stress-strain loop is not much greater than at ordinary temperatures, and is less than that given by an annealed tube. But if the cycle takes a quarter of an hour, the dissipation is increased four-fold. On the other hand, in the annealed tube at 300° C, the energy lost per cycle of stress is still almost independent of the time.

At a higher temperature, for example at 540° C., the hard-drawn tube flows rapidly and continues to flow for a long period, though at a diminishing rate, under a shear stress of less than 1 ton per square inch. Moreover, again like pitch or glass, the steel at this temperature shows considerable elastic afterworking. If the stress be suddenly removed the immediate elastic recovery is followed by a slow backward flow which persists for many minutes. Some

flow and elastic afterworking were also observed in the annealed tube at this temperature, but both were much less than in the hard tube.*

Apparatus.

The apparatus was an improved form of the static apparatus described in 'Roy, Soc. Proc.,' A, vol. 89, p. 537, and the method of obtaining the area and shape of the hysteresis loop has been explained there.

The experimental tube was rigidly fixed at one end to a much longer and stronger hard tube. The stiff tube was rigidly fixed at one end, and the torque was transmitted to it through the experimental tube, the twist in the stiff tube providing a means of measuring the torque.

Fig. 1 gives a general view and details of the apparatus. The compound tube GH was rigidly fixed at G, and the end H securely fixed to lever L, which worked between adjustable stops E and F. By movement of this lever any desired stress could be applied.

Sensitive micrometer levels were fixed to the tubes in the positions A, B, C, D, and at M₁ and M₂ small concave mirrors were arranged in conjunction with lamp and scales S₁ and S₂. The weights W exactly balance the weight of lever L. The mirrors in conjunction with scales supply the means of measuring extreme ranges of strain and thus of stress.

The tube was heated by passing an alternating electric current through the tube itself, and the temperature of the tube was ascertained by three thermocouples in conjunction with galvanometer J and scale. The current was led into and from the tube by means of small arms dipping into mercury baths, a mode of connection which did not exert appreciable force on the tubes.

It was found by experiment that by taking a tube sufficiently long, a fairly uniform temperature could be maintained along the central portion of the experimental tube. Three thermo-couples were brazed to the tube at points 6 inches apart, and these showed a variation of 3° or 4° C. at 500° C., the ends being below the centre in temperature. The mirrors were set 8 inches apart, so that, for the length under observation, the temperature has been taken as that given by the central thermo-couple.

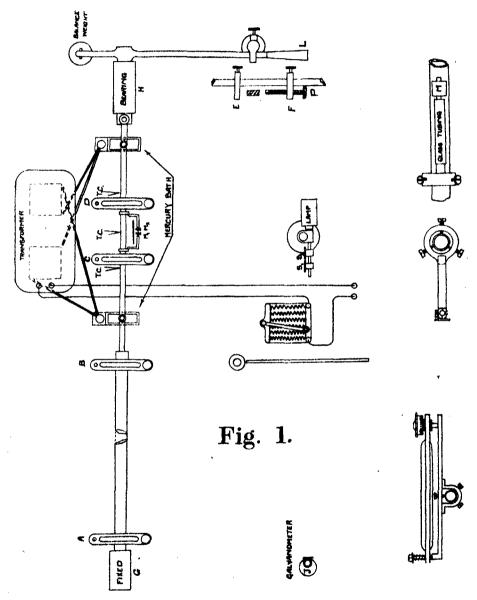
The thermo-couples were calibrated by observing the melting points of pure metals, and temperatures given may be taken as true to within 2° C.

The heating current was taken from a transformer, the secondary circuit consisting of four coils arranged in parallel, each sending its current through the tube. The temperature was readily regulated by external resistances in

* Hopkinson and Rogers found considerable elastic afterworking in steel at 600° C. and upwards after applying and removing a load of 1½ tons per square inch ('Roy. Soc. Proc.,' A, vol. 76, p. 419 (1905)).

the primary circuit, a resistance slide giving a delicate means of adjusting the current to give any desired temperature.

An electromotive force ranging from 20 to 200 volts by steps of 20 volts



could be applied to the primary circuit, which together with adjustable resistances above mentioned allowed any temperature between that of the room and 600° C. being maintained for any period of time.

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To obtain a uniform temperature along the tube all the heat was allowed to radiate freely to the atmosphere, no lagging being used. The mirrors were protected from radiation by reflectors, and heat was prevented from conduction to them by supporting them at the ends of glass tubing as shown in fig. 1.

The steel tubes had the following chemical composition:—Carbon 0.17 per cent.; manganese, 0.24 per cent.; sulphur, 0.02 per cent.; phosphorus a trace, the remainder being iron.

The tubes as supplied by the makers were hard as the result of the drawing. The elastic limit in torsion in this state was 13.8 tons per square inch shear stress in either direction, giving an elastic range of 27.6 tons per square inch.

By annealing at 800° C. for 15 minutes and cooling in an electric furnace, the effect of the drawing was removed. The tubes were then quite soft and ductile and had a well marked yield point in torsion of 5.58 tons per square inch shear stress, giving an elastic range of 11:16 tons per square inch.

Hysteresis Experiments.

A hard-drawn tube was introduced into the apparatus and subjected to a stress range of 8.32 tons per square inch (± 4.16 tons per square inch); 200 cycles between these limits were performed to bring the tube into a cyclic state, and the stress was reduced approximately to zero by bringing the lever L into the central position. The micrometers were then adjusted to make the levels A and B both read zero. The load was then applied and removed, thus completing another half-cycle of stress, and the stress again adjusted by movement of lever L until the levels A and B again read zero. The effect of this procedure is to bring the stress in the thin tube to exactly the same small value that it had before the half-cycle was performed, but this condition has been approached from the opposite direction and the strain is slightly different by reason of the elastic hysteresis. This change of strain is shown by a small difference in the movements of the levels C and D which have occurred as the consequence of the half-cycle of stress. The following results were obtained for the above stress range:—Movement of C 0.3, movement of D 2.1, and the difference, 1.8, is a measure of the elastic hysteresis.

The tube was then heated to 100° C. and 100 cycles were performed at this temperature. The result was:—Movement of C 0.3, movement of D 2.2, and the difference, 1.9, is greater than before by a small but unmistakable amount. The above cycles were performed at the rate of 5 seconds per cycle.

A slow cycle was next performed lasting in all 2 hours, the temperature of the tube being maintained at 100° C. The hysteresis was found to be exactly the same as in the quick cycle, namely, 1.9. The experiment showed that the

hysteresis increased slightly with temperature up to 100° C., but was still independent of the time. At temperatures in the neighbourhood of 200° the hysteresis was greater when the cycle was performed slowly, the material showing some signs of flow.

Table I gives the results obtained with stress range throughout of 11.60 tons per square inch (± 5.8 tons), this stress being well within the elastic limit as ordinarily measured.

	Thermo-couple temperatures C.			Movements of levels.		Difference = hysteresis.
	1.	2.	3.	C.	D.	- Hysocronia
Value cold	19	19	19	0.8	3.3	2.5
Cycle performed in 5 secs.	194	198	196	0.8	4.15	3 .35
, 16 mins.	195	199	198	0.9	4.70	3.8
Cycle performed in 5 sees.	227	230	225	1.0	4.8	8.8
,, 16 mins.	227	229	225	1.1	6.7	5.6
Cycle performed in 5 secs.	290	294	289	1 1	6.0	4.9
" " 16 mins.	290	294	291	2 .0	28 '7*	21 .7
Value cold after above	19	19	19	0.8	3 .3	2 . 5

Table I (Stress Range, 11:60 tons per square inch).

Hard-drawn Tube.

The above Table shows that, at temperatures above 200° C., time is an element in the stress-strain relation. It also shows that the tube was not changed in structure appreciably by being so treated, since, when allowed to cool, the hysteresis returned to its normal value. In the paper previously referred to it was pointed out that the hysteresis of a hard-drawn tube was increased about eight-fold by annealing at 800° C. and cooling in the furnace.

Flow Experiments.

At temperatures above 300° C, the flow became too great for measurement by the spirit levels and the strain was read direct by means of the mirrors. The levels B and C were used for measuring stress, level B being adjusted to read zero when the tube was subjected to a definite stress, and level C being placed on the large tube near level B and adjusted to read zero when the tubes were free from stress. In making an experiment the large tube was first released from stress by releasing the fixed end. Level C was then adjusted to read zero, and the large tube fastened down at the fixed end. A stress was then applied and its amount calculated from movements of mirrors. Level B was adjusted to read zero with the stress

^{*} Equivalent in level motion. Micrometer head used for measurement.

applied. To keep the tube while flowing at a constant stress it was only necessary to adjust lever L so as to keep level B at zero. The tube could be freed from stress by adjusting lever until level C read zero.

Throughout the tests described below the tube was subjected to a constant shear stress of 0.79 ton per square inch. The application of the stress and its adjustment to the desired value took about half a minute, and a similar time was occupied in removing the stress and adjusting it to zero.

Time from	St.	,	Scale re	Difference = strain.	
start. Stress.	Temperature.	M ₁ .	M ₂ .		
mins. O] Stress being		840	320	
± 2	spplied Stress on		299 ·5	268 -25	11 .25
20	Stress being	887° C.	2 97 · 5	265 .25	12 .25
201	removed Stress off		339	818	1.0
25	J		889	818 .25	0.75

Test I.—Tube Unannealed (Stress = 0.79 ton per square inch).

At this temperature the strain which develops in 20 minutes after the application of the stress is about one-tenth of the initial elastic strain, and about one-quarter of this flow is recovered after removing the stress, leaving three-quarters as permanent set.

Time from start.	Stress. Temperature.	415	Scale :	Difference	
		1 emperature.	М,.	M ₂ .	- strain.
		Test II.	AND THE PERSON NAMED IN COLUMN		
mins. 0 2 4 6 8 10 15	Stress being applied Stress on	894° O.	342 297 · 5 296 · 6 295 · 7 295 294 · 5 294 298 292	821 264 · 5 263 261 · 8 280 · 7 260 259 · 8 257 · 7 256	12 °0 12 °6 12 °9 13 °8 13 °5 14 °3 16 °0
20½ 21 22 24	Stress being removed Stress off		836 · 5 887 · 1 887 · 5 837 · 8	812 ·5 818 · 6 814 · 8 814 · 9	8·0 2·5 2·2 1·9

Time from	Stress.	Temperature.	Scale	readings.	Difference
start.		Temperature.	М1.	M ₂ .	= strain
		Test III.			The state of the s
mins, O	Stress being applied		887	315 .5	İ
1 2			291 · 8 290 · 5 289 · 8	256 ·5 253 ·8 250 ·5	18 ·3 15 ·2 17 ·3
3 4 5			288 · 2 287 · 2 286 · 3	248 ·8 246 ·5 244 ·9	18·4 19·2 19·9
6 7 8	Stress on		285 · 5 284 · 8 284 · 2	243 ·6 242 ·5 241 ·5	20 · 4 20 · 8 21 · 2
10 12 14		442° C.	288 282 281	289 -6 288 286 -6	21 ·9 22 ·5 22 ·9
16 18 20			280 ·1 279 ·2 278 ·5	285 ·4 284 ·2 283	28 · 2 23 · 5 24
201 21	Stress being removed		324 ·2 825	292 298 ·2	10·7 10·8
22 28 24	Stress off		826 ·5 827 ·5 828	295 ·5 297 297 ·7	9·5 9·0 8·8
25)		328 ·2	298 0	8.7
0 1		Test IV.	***		
1	Stress being applied		829 ·5	298 .5	
1	Ì		275 · 5 271 · 0	227 ·5 220	17 20·5
2 8			264 259 · 5	209 ·5 202 ·25	23 · 5 26 · 25
4 5	**		256	197	28
6			253 251	192 · 5 189	29 · 5 81 · 0
7 8	Stress on		249	186	82 .0
10			247 244	183 178	88 0
12 14		492° C.	241	178 -5	36 .2
16			238 ·6 236	170 166	87 ·5
18 20	Stress hairs		284 282	162 ·5 159	40 ·5 42
201 21	Stress being removed		286 290 5	230 287	25 22 · 5
22 23	Stress off		298 5 295 5	241 · 5 244 · 5	21 20
24 25			297	247	19
26	}		298 298 •5	248 · 5 249 · 75	18 · 5 17 · 75

Time from start.	a,	m	Scale r	eadings.	Difference - strain.
	Stress. Te	Temperature.	М ₁ .	\mathbf{M}_2 .	
age to the second section of the second section of the second section of the sec		Test V.			
mins. 0 1 1 2 8 4 5 6 8 10 12 14 16 20 20 12 21 22 23	Stress being applied Stress on Stress being removed	542° C.	282 279 274 · 5 271 268 265 263 259 255 · 5 251 · 5 249 245 302 308 309 310 · 5	289 227 · 5 216 208 201 196 191 183 176 170 · 5 166 162 155	24 5 83 0 40 0 44 5 48 5 50 5 53 5 61 0 64 5 67 0 68 5 71 5
24 25	J		311 ·25 312 ·0	248 249 · 5	44 .75

Test VI.—The tube after Test V was lowered in temperature to 491° C., that is to approximately the temperature of Test IV, and records were taken of the flow under the same stress.

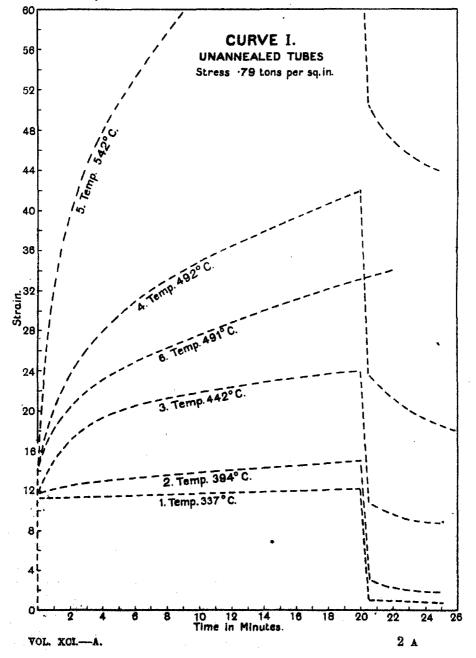
The following Table shows the results, and (in the last column) the amount

Test VI.

Time from start. Stress.	94	Tempera- ture.	Scale	Scale readings.		From
	Stress.		M ₁ .	M ₂ .	= strain.	Test IV
mins. 0 1 2 4 5 8 11 13 16 20	Being applied Stress on	491° C.	36 · 5 84 · 0 88 90 93 94 96 · 2 98 · 5 100 101 · 8 105 · 5	-38.5 25.5 31.2 35.2 41 43 47.6 51.7 54.5 63.5	16 · 5 18 · 2 20 · 2 23 24 26 · 4 28 · 2 29 · 5 30 · 7 38 · 0	16 · 9 20 · 8 23 · 3 27 · 7 28 · 2 32 · 6 34 · 8 36 · 6 37 · 6

of flow observed at corresponding times in Test IV when the temperature was the same, correction being made for the 1° C. difference in temperature.

The difference is probably due to the annealing effect of Test V (during which the tube was kept at 542° C. for half-an-hour), which would make the metal more crystalline and less liable to flow.



Test VII.—An experiment was performed at 600° C. upon the same tube as Test VI and the following values were obtained:—

Test VII.

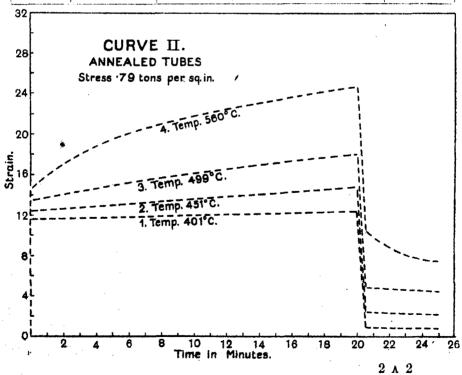
Time from start.	Stress.	Strain.	Temperature.
mins. 1 5 10 15 20 20 20 25 30	Stress on 0.79 ton per square inch	85 62 781 91 98 801 731 72	600° €.

Experiments with Annealed Tube.

The tube was annealed by heating it to 800° C. in an electric furnace for 15 minutes and allowing it to cool in the furnace. The stress for annealed tubes was the same as that for unannealed tubes, namely 0.79 ton per square inch.

Time from start.	(T)	m	Scale	Difference	
	Stress.	Temperature.	М1.	M ₂ .	= strain.
P	, yet digitalerinian susuapa value .	Test	I.	,	•
mins.		1.	17 5	-21.5	
U	Being applied		0		
1	,		54 · 5	27	11.6
10	Stress on		55	28	12 0
20	ί	401° C.	55 ·5	28 '8	12 .8
001	Being removed		10.#	10.7	0.8
201	Strong of		18 · 5	-19.7	0.48
25	Stress off		18 .4	-19.9	0.7
		Test	II.		
0			18 0	-20.5	1
•	Being applied				
1	1		56 ·5	80 4	12.4
10	Stress on		59 0	34	18 6
20	1 2	451° C.	61 ·1	87 .8	14 7
201	Being removed		22 •6	-13.6	2.8
203	Stress off		an u		
25]		22 .5	-13.9	2.1

Time from			Scale	readings.	Difference
start.	Stress.	Temperature.	\mathbf{M}_{1} .	M ₂ .	- strain.
	***************************************	Test 1	П.	and the state of t	**************************************
mins.	•		10.5		1
0	7 70-1		18.5	-21	
1	Being applied		59 .2	33 .2	13.5
10	} Stress on		62 .8	39.8	16.0
20	I paroun on	499° C.	65 . 5	48.9	17.9
20	Being removed	400 0.	00 0	300	1.0
201	J Doing Tomoved		24 .5	-10.1	4.9
201	} Stress off		## U	1 .0 .	7.0
25	J 50.000 0A		23 .9	-11.2	4.4
		Test 1	IV.		
0	١,	1	34·5	-5.7	1
	Being applied				
ł	1		75 ·6	80 6	15.2
2			77 ·5	54 .5	17 .2
5			80 0	59 -8	19 .5
2 5 8	Stress on		81 •7	62 .6	21 ·1
10		560° C.	82 ·6	64 2	21 .8
15		500 O.	84 8	67 .7	23 .3
20	ፈ		86 • 8	70.6	24.5
	Stress being re-			!	
201	moved		45 2	15.5	10.8
22	L _		42 5	11 0	8.7
28	Stress off		40 .8	8.6	7.9
25	,		88 88	6.0	7.4

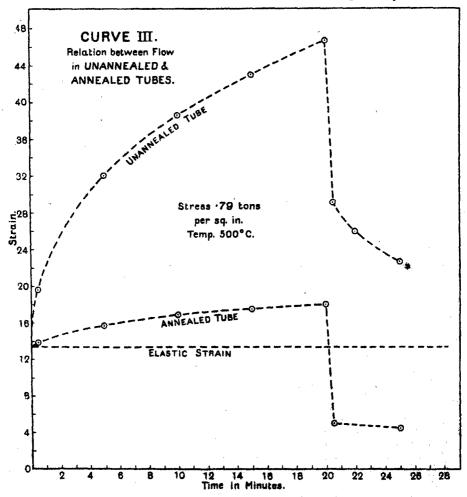


302 Elastic Properties of Steel at Moderately High Temperatures.

In the following Table the flow and recovery of the annealed (S) and unannealed tubes (H) at the same temperature are compared. The figures are corrected by interpolation from the results given in the above Tables to reduce them to the same temperatures.

	Unannealed tube (H).	Annealed tube (8).
Temperature	500° C.	500° €.
Probable elastic strain*	13 ·8	18 .8
Strain after minute	19 .7	18 ·8
Flow in 20 minutes	88 .4	4.7
Recovery in 41 minutes	6.2	0.55
Stress	0.79 ton per square inch	0 79 ton per square inch

The elastic strain is that corresponding to an instantaneous application and removal of the load, and is calculated on the assumption that the elastic modulus falls 5 per cent. per 100° C.



The above work was carried out in the Engineering Laboratories of Cambridge University, and I wish to express my sincere thanks to Prof. B. Hopkinson for his many suggestions and inspiring interest.

A Chemically Active Modification of Nitrogen, produced by the Electric Discharge.—VI.*

By the Hon. R. J. STRUTT, Sc.D., F.R.S., Professor of Physics, Imperial College, South Kensington.

(Received March 9, 1915.)

§ 1. Effect of Catalysts in Promoting the Formation of Active Nitrogen.

There has been considerable controversy on the question of whether or not pure nitrogen would give the afterglow, which, as I have shown in the previous papers of this series, is associated with the presence of chemically active nitrogen.

E. P. Lewis† was disposed to think that the presence of oxygen or nitric oxide was essential, but in a much later paper, though still inclined to the same opinion, he states that the afterglow continually increased in intensity as the proportion of oxygen was reduced.

Warburg, in some experiments on the "luminous electric wind" in nitrogen at atmospheric pressure, found that the intensity of the effect was much diminished by prolonged heating with sodium at 300° C., though he expressly states that he was unable to get rid of it altogether. It is not clear that the "luminous electric wind" (which was not bright enough for adequate spectroscopic examination) is the same phenomenon as the active nitrogen glow obtained at low pressures. Experiments made later in Warburg's laboratory by von Mosengeil on the active nitrogen glow at low pressure led to the conclusion that it was not diminished by heating the gas with sodium in a closed discharge vessel.

^{*} I, 'Roy. Soc. Proc.,' A, vol. 85, p. 219; II, 'Roy. Soc. Proc.,' A, vol. 86, p. 56; III, 'Roy. Soc. Proc.,' A, vol. 86, p. 262; IV, 'Roy. Soc. Proc.,' A, vol. 87, p. 179; V, 'Roy. Soc. Proc.,' A, vol. 68, p. 589.

^{† &#}x27;Astrophys. Journ.,' vol. 12, p. 8 (1900); 'Ann. der Phys.,' vol. 2, p. 249 (1900); and also 'Astrophys. Journ.,' vol. 20, p. 49 (1904).

^{† &#}x27;Phil. Mag.,' June, 1913, p. 326.

^{§ &#}x27;Ann. der Phys.' [4], vol. 10, p. 180 (1903).

^{|| &#}x27;Ann. der Phys.' [4], vol. 20, p. 838 (1906).

In my own earlier experiments in which the presence of chemically active nitrogen was first demonstrated,* I employed various methods of preparing nitrogen, but obtained no indication that anything else than nitrogen was essential.

F. Comtet found that after very prolonged passage of nitrogen over hot copper a gas could be obtained which did not give the glow, and he was able to restore the glow by admission of minute quantities of oxygen.

Attempts were made by Koenig and Elöd‡ and by myself§ to repeat Comte's result, but without success. I had, indeed, frequently used hot copper purification before that time, and obtained the glow as usual.

In the note cited I described a technique of purifying nitrogen for this work by prolonged contact with cold phosphorus. It was made practically certain that such nitrogen could not contain one part of oxygen in 100,000, for admission of oxygen to that extent distinctly restored the luminosity and cloud formation which attend oxidation of moist phosphorus.

Shortly after Comte's publication E. Tiedell published some experiments which he regarded as confirming Comte's conclusion. Passing over these, which were not very strongly emphasised, we come to a publication of Tiede and Domcke describing the preparation of nitrogen from barium or potassium azide. They found that nitrogen thus prepared gave no glow, but that the glow could be restored by admission of a trace of oxygen.

This experiment was repeated by Koenig and Elöd** and by myself, in collaboration with Prof. H. B. Baker.†† In each case the opposite conclusion to that of Tiede and Domcke was recorded. Prof. Baker and I also introduced the liquid alloy of sodium and potassium into a sealed vacuum discharge vessel containing rarefied nitrogen. The glow remained very bright even on prolonged standing. Tiede and Domcke in a third paper‡‡ returned to the use of hot copper. Bomb nitrogen was passed over copper heated to about 400° C., and the glow was almost completely got rid of. At high temperatures it returned, a result attributed to dissociation of any copper oxide that might be formed. No drying agents or other absorbents were used.

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* I, of this series.

† 'Phys. Zeits.,' vol. 14, p. 74 (1913).

† 'Phys. Zeits.,' vol. 14, p. 165 (1913).

§ 'Phys. Zeits.,' vol. 14, p. 215 (1913).

() 'Berichte,' vol. 46, p. 340 (1913).

** 'Berichte,' vol. 47, p. 523 (1914).

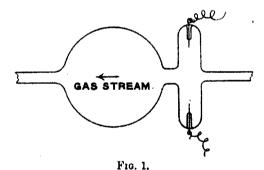
†† 'Berichte,' vol. 47, p. 801 (1914).

‡‡ 'Berichte,' vol. 47, p. 420 (1914).
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Prof. Baker and I were unable to repeat this result.* The glow occurred admirably with the copper at any temperature up to a red heat.

Finally, J. de Kolowski, working with the electrodeless discharge, obtained the glow as usual with nitrogen which had been purified from oxygen by means of potassium.

Tiede and Domcke argued from their experiments that there was no such thing as active nitrogen. The palpable weakness of this reasoning, combined with the failure of Prof. Baker and myself to confirm either of the experiments which were described as so easy and certain of repetition. obscured from us the real value of their work. This was not realised until Tiede and Domcke came to London with their apparatus and materials and repeated their azide experiment at the Imperial College. The glow was much reduced, though (at all events in all the experiments made on this occasion) it was still conspicuously visible; when a trace of oxygen was admitted by heating a little silver oxide enclosed in the apparatus, the glow was restored. These results were obtained with a discharge tube like that illustrated in my first paper. Using a discharge tube like that shown in fig. 1, which has a large bulb in which the glowing gas accumulates, we did



not succeed in diminishing the glow much, if at all. These experiments were described jointly by Baker, Tiede, myself and Domcke.

During this visit a further attempt was made by Prof. Baker and myself,

- * 'Berichte,' vol. 47, p. 1049 (1914).
- † 'Comptes Rendus,' vol. 158, p. 625, March 2, 1914.

^{.‡} The glow associated with the presence of active nitrogen is not obtained from ordinary nitrogen unless a trace of oxygen is present: therefore there is no such thing as active nitrogen—such was their argument. To obtain a clear view of the value of this kind of reasoning, apply it to the following more familiar case. Formation of sodium chloride by the interaction of sodium and chlorine is not observed unless a trace of moisture is present: therefore there is no such thing as sodium chloride.

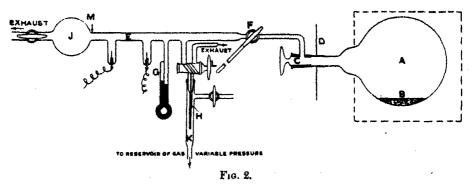
[§] I, p. 228.

^{| &#}x27;Nature,' vol. 93, p. 478 (1914).

with the benefit of such suggestions as Tiede and Domcke could make, to repeat their experiment with copper moderately heated, but with the same ill success as before. Dr. Tiede, if I understood him rightly, regarded the failure as due to some difference of our copper or crude nitrogen from that used by him in Berlin; but exactly what difference he was unable to say. During a brief visit it was impossible to go into the matter further.

After these joint experiments I felt that the position of the question was very unsatisfactory. For, though now convinced that it was possible to prepare nitrogen which would give a much increased glow when oxygen was added to it, my previous conviction was unshaken that the phosphorus-purified nitrogen above mentioned, which gives the nitrogen glow excellently, did not contain oxygen to the extent of 1 part in 100,000.

It might, indeed, be possible to get out of the difficulty by assuming, with Tiede and Domcke, that almost incredibly minute quantities of oxygen were sufficient; but I soon found experimentally that this was not the case. In taking up the matter again after Dr. Tiede's visit, I sought to avoid the use of azide, the preparation of which in any quantity is troublesome and unpleasant, and not altogether free from risk. It was found that a sample of nitrogen which did not give much glow could be prepared by prolonged treatment of the commercial bomb nitrogen with sodium or potassium at 300° C. A flask A, fig. 2, of about 4 litres capacity, contained 10 or 20 c.c. of



the liquid alloy of sodium and potassium.* The flask was in an asbestos oven (shown by dotted lines), with an electric resistance heater on the bottom. The flask was supported about an inch above the heater, and the temperature just under it was somewhat over 300° C. The lid of the oven was thin, so that the top of the flask was by no means so hot as the bottom, where lay the pool of alloy B. Thus a good circulation of the gas over the surface of

^{*} This was introduced by means of a pipette, after the flask had been filled by displacement with bomb nitrogen.

the alloy by convection currents was assured. Some of the metal distilled on to the top of the flask, and also into the neck, which was necessarily kept cold, because of its greased stopcocks. A tin screen, D, in two semi-circular halves, carried on the neck, protected the latter from radiation.

Bomb nitrogen was admitted to this flask at a reduced pressure, so that on heating the pressure did not rise above the atmospheric. The heater was turned on after the gas had been admitted, and left on all night. In the morning the gas was allowed to cool, and was ready to be passed through the vacuum discharge tube E on its way to a Gaede pump. The regulating stop-cock F and the pressure gauge G enabled the pressure in E to be kept at a standard value of 6 mm., in spite of the gradual reduction of pressure in A during the experiment. Under these circumstances, the gas passing out through the pump measured 2600 litres per hour. A constant jar discharge was maintained between the platinum electrodes. The R.M.S. current measured on a Duddell thermo-ammeter was 7 milliampères.

Under these conditions the nitrogen afterglow was not bright, and it seemed to get dimmer still after a charge of the alloy had been heated several times with successive fillings of nitrogen. The glow still remained visible both in the neck and in the body of the bulb J. But it was reduced as low, or lower, than in the most successful experiment which Tiede and Domcke had shown us. Although the glow was feeble, there was no indication that what there was of it died out sooner than usual, as the stream of gas passed along the tubes leading to the pump. The proportion of oxygen necessary to get the optimum glow was investigated by means of the capillary inlet tube H,* by means of which air could be admitted. The capillary drew its supply from the outer tube K in which it was placed. K was connected with a large reservoir. The rate of intake could be adjusted by altering the air-pressure in this reservoir. Its exact value under given conditions was determined after the experiment by observing, with the manometer, the rate at which the pressure rose in the vacuum tube E, the volume of which was known.+

The stopcock used to shut off the capillary inlet at pleasure is necessarily made of much wider bore tubing than the capillary itself. Thus there is a considerable dead space between the capillary and the stopcock. Without

^{*} The various capillaries used were drawn out in the blowpipe. After a little practice, capillaries can be drawn giving approximately the rate of intake desired. A special apparatus was used for testing them rapidly. Preliminary inspection with a magnifier is useful.

[†] With a capillary of non-uniform bore the intake of air into a vacuum bears no simple relation to the feeding pressure. Hence the necessity for determining it directly at each pressure.

special arrangements this would fill up with air when the stopcock was shut, and the accumulation would suddenly pass in when it was opened again, thus disturbing comparative observations. The difficulty was avoided by using a two-way stopcock as shown at L. When the flow through the capillary was not directed into the apparatus, the dead space was kept exhausted by a supplementary air pump, connected to the other branch of the two-way stopcock. When it was desired to observe the effect of admitting air, the stopcock was quickly turned through 180°, and the normal rate of inflow was at once established.*

A capillary was used which allowed 18 c.c. of air (measured at N.T.P.) to enter into a vacuum per hour from a reservoir at atmospheric pressure. This is equivalent to about 3.5 c.c. of oxygen per hour. By substituting pure oxygen for air, the rate of admission could be increased. By rarefying the air it could be diminished. In this way the following results were obtained:—

Oxygen admission.	Intensity of glow.
c.c. per hour.	1
0.0	Faint.
0 .4	No perceptible increase.
1.0	No perceptible increase.
8 -5	Strong glow.
18.0	No further increase.

It appears, then, that an admission of 3.5 c.c. of oxygen per hour produced about the maximum effect. Since the nitrogen flow was 2600 c.c. per hour, this represents an oxygen concentration of about 1/750 of the whole. If the oxygen admission is increased much beyond the quantities given in the Table, it begins to have a prejudicial effect. About 2 per cent. of it is enough to destroy the glow altogether.†

It appears, then, that in mixtures of nitrogen with oxygen the optimum effect is got when the oxygen present is something rather over one part in a thousand. Yet it had been clearly shown that nitrogen purified from oxygen by prolonged standing over phosphorus could not contain oxygen to the extent of one part in a hundred thousand, and yet nitrogen thus purified

^{*} An alternative method, useful when direct intake from the atmosphere is desired, is to close the capillary with an indiarubber pad, brought up from below by a rack movement. In this case there is no dead space. When working with these very narrow capillaries it is necessary to be constantly alive to the possibility that they have become plugged by specks of dust.

[†] See V, p. 541.

gives the glow as well, or even better than nitrogen purified with hot sodium, to which the optimum percentage of oxygen has been added.

Minute admixtures other than oxygen are capable of performing the same function, and can act as catalysts for promoting the formation of active nitrogen by the discharge.

This was established by means of the apparatus already described, other gases being introduced into the tube from which the capillary drew its supplies. In these experiments I did not attempt to determine the optimum percentage of each admixture. A capillary was used admitting 3.3 c.c. of air per hour. The rate of admission of other gases by this tube would be somewhat different, depending upon the viscosities, which, however, do not vary widely. Roughly speaking, this capillary admits about 1/1000 part of foreign gas to the nitrogen stream under the standard conditions adopted.

It is to be observed that the purity, or dryness, of the added gas is not of the first consequence, since the total admission is so small. Impurity in it, in fact, only enters into the second order of small quantities. Still, reasonable care was taken.

Methane, from aluminium carbide: strong restoration of glow. The quantity admitted was enough to slightly tinge the nitrogen afterglow with violet of the cyanogen spectrum, owing to reaction of methane with active nitrogen after the latter is formed. If the admission was stopped, the glow passed through a brilliant yellow stage of simple afterglow spectrum as the percentage of methane diminished, and then became very dim as the methane was eliminated. By experiments in which the feed of methane was at reduced pressure, it was found that 0.09 c.c. of methane per hour, 1/30,000 of the nitrogen flow, was enough to produce a perceptible effect.

Ethylene from sulphuric acid and alcohol, and Acetylene from calcium carbide, gave the same results as methane.

Carbon Monoxide from potassium ferrocyanide, washed with potash, strongly restored the glow, which was yellow, showing only a faint trace of cyanogen spectrum.

Carbon Dioxide induced a strong and pure nitrogen afterglow.

Sulphur Dioxide did the same.

Hydrogen Sulphide induced a specially bright and pure yellow nitrogen afterglow. When the entrance of hydrogen sulphide was stopped, it was not found that the glow passed off at all quickly or easily. Indeed, to reduce it to the point reached before admission of hydrogen sulphide, the tube had to be dismounted and washed out with aqua regia. It seems that exceptionally small traces of sulphur are sufficient to induce formation of active

nitrogen. These traces cling about the apparatus, probably in the solid state, with great obstinacy.

Chlorine, purified by fractional distillation of liquid chlorine, gave an absolutely definite though not very strong restoration of the glow. This case is peculiar, in that the glow restored by chlorine is notably greener than that obtained in other cases. The spectrum is the same as usual, but the yellow band is less intense relative to the green one. It is intended to study the question further, but it would seem as if chlorine atoms must remain in some kind of association with the atoms of active nitrogen, damping the vibrations which give rise to the yellow band. It takes time to get rid of this green tint. The chlorine seems to hang about the apparatus persistently.

Hydrogen was prepared from pure zinc and sulphuric acid, and freed from condensable impurities such as arsine, by passing through a tube packed with copper gauze and maintained at -180° C. in liquid air. It was thought that a definite effect was produced in increasing the glow, but it was slight and difficult to observe, being much less in amount than in any of the previous cases.

Argon and Helium, each carefully purified, gave no observable effect.

The method of regulated admission by a capillary tube, so far used, is not easily applicable, except to permanent gases.

In addition, I have tried water vapour and mercury vapour, but the exact rate of admission was not measured in these cases.

A drop of Mercury was placed in a side tube, so that by warming it could be made to give off vapour which mingled with the nitrogen stream. Marked restoration of the glow was observed, though it was less brilliant than that observed with the best catalysts. The glow was tinged with green from the green mercury line, but, apart from this, there was marked brightening of the true nitrogen afterglow bands. The glass all round the mercury was carefully heated, so as to get rid of all adherent carbon dioxide or water vapour, and the effect of warming the mercury was repeatedly observed. There is no doubt of the fact that the restoration is really due to mercury.

A drop of Water in a side tube was frozen in liquid air. As its temperature was allowed to rise very strong restoration of the glow was observed. The quantity of vapour soon became excessive and the glow diminished again, until it was destroyed altogether.

The relative efficiency of the various admixtures in inducing the nitrogen glow cannot be very satisfactorily compared, since no attempt was made to adjust each to its exact optimum amount, nor were any photometric measurements made. However, the following roughly approximate list

represents my general impressions. The most effective substances are placed first:—

Hydrogen sulphide.	Oxygen,
Water.	Mercury.
Carbon dioxide.	Chlorine.
Carbon monoxide.	Hydrogen
Acetylene.	Argon.
↓ Ethylene.	$\begin{cases} \mathbf{Argon.} \\ \mathbf{Helium.} \end{cases}$
Methane.	Nitrogen.

It is then established that to obtain active nitrogen at all abundantly, it is necessary that a quantity of some foreign gas should be present to the extent of something like 1/1000 part. This gas may be oxygen, or some compound of oxygen, but it may as well, or better, be sulphuretted hydrogen. Thus it is perfectly clear that, whatever the function of the admixture may be, oxidation of nitrogen has nothing to do with it.

In the controversy which has been reviewed it was maintained, on the one side, that pure nitrogen would give the full effect, and, on the other, that the presence of oxygen was essential. It is now seen that, as in so many previous scientific controversies, neither side was entirely right. Almost any contamination, with the exception of argon and helium, increases the yield of active nitrogen, as judged by the intensity of the nitrogen afterglow.

To exactly explain why each of the numerous experimenters quoted got the result he did would be too ambitious an attempt. At the best there would be a large element of conjecture in it which could not be checked experimentally. But a few suggestions may be offered. Methods of purification, designed chiefly to remove oxygen, may result in the unintentional introduction of other substances which have the same effect in producing the glow that the oxygen itself had. Carbonaceous impurities are, perhaps, the most likely to be concerned; indeed I have frequently observed, particularly at high pressure, a trace of violet cyanogen in the nitrogen afterglow, when there was no other special reason to suspect the presence of carbon. Unless my memory deceives me, this was observed in those experiments with azide nitrogen in a large globular discharge-vessel, made on the occasion of Tiede and Domcke's visit. Visible cyanogen spectrum implies the presence of more than enough hydrocarbon to act as a catalyst and induce the glow. grease of stopcocks may sometimes act as a source of carbon, particularly when stray electric discharges come in contact with it.

In experiments where oxygen is removed with hot copper, I suspect that carbon dioxide is very apt to remain in the gas. Thus, in one attempt to

repeat Tiede and Domcke's experiment with copper at 400° C., the copper gauze employed had originally contained a great deal of paraffin oil used as a lubricant in the wire-drawing process. This was removed, as far as possible, by heating and oxidising the copper, which was afterwards reduced by plunging it in methyl alcohol and drying it in warm air. It would require special tests directed to that end to make absolutely sure that no carbonaceous matter remained after this treatment. If there was a trace, it would be oxidised by traces of oxygen in the nitrogen used, thus introducing carbon dioxide.

The gas which had stood over moist phosphorus also contained carbon dioxide, as was proved by bubbling it through baryta water. The amount of precipitate was decidedly more than the same volume of air gave under similar conditions, and thus indicates something like 1/1000 part of carbon dioxide, just such a quantity as would give the glow well. I have not particularly examined where this carbon dioxide came from—it is enough for the present purpose that it was there. In all probability phosphorus vapour would also induce formation of active nitrogen, though I have no definite evidence of the fact.

As regards earlier attempts to get rid of the glow by treatment with sodium or potassium: if the metals have been stored in oil (as potassium almost always is) enough hydrocarbons will probably cling to them to explain such experiments as that made by Prof. Baker and myself, allowing nitrogen to stand over the cold liquid alloy. But in any experiments on vacuum tubes charged with gas, and sealed up, the quantity of nitrogen present is so small that the absolute quantities of impurity needed are infinitesimal, and may be derived from the electrode or the glass. When a large quantity of nitrogen is purified and allowed to sweep through the apparatus, this source of contamination is practically eliminated.

These questions cannot be discussed in more detail, for lack of space. But, in short, it is easy to understand that methods designed to get rid of oxygen do not in general get rid of carbon compounds. The prolonged use of very hot sodium, however, is capable of removing both.

§ 2. Probable Mode of Action of the Catalysts.

If it is considered how diverse chemically the different catalysts are, it will not seem likely that their action can be interpreted by purely chemical considerations. We must remember that the impurity added performs its function, whatever that may be, inside the region where the electric current is passing. It is useless to add a trace of, e.g., oxygen after the stream of

nitrogen has left the discharge, for in that case the addition produces no effect in increasing the yield of active nitrogen.*

The question is essentially one of processes occurring in the electric discharge, and must be considered in the light of our knowledge of the properties of electrons and gaseous ions.

In this connection the results of Franck[†] are very suggestive. He investigated the velocity with which negative ions travelled through nitrogen at atmospheric pressure, under potential gradients far too small to produce luminous discharge. It was found that with perfectly pure nitrogen the velocity was very large, indicating that the ions travelled over the greater part of their path as free electrons. A small admixture (something like 1 per cent.) of oxygen or chlorine diminished the mobility of the negative ions two hundred-fold, and made it about equal to that of the positive ions. In short, in pure nitrogen the negative ions were free electrons: the addition of a trace of oxygen or chlorine loaded them so that they became of atomic dimensions. Argon and helium, even when present in much more than traces, were unable to produce this effect.

Another property of pure nitrogen, namely, its capacity to yield active nitrogen under the discharge, is also extraordinarily influenced by a trace of oxygen or chlorine, but not by argon or helium. Can it reasonably be doubted that there is an intimate connection between the two sets of phenomena? That the properties of a substance should be modified in this way by a large multiple when slightly contaminated is always surprising and exceptional. When we find two such cases running parallel, as these do, the suspicion of some connection becomes very strong.

^{*} It is possible that someone casually glancing at this paper without being acquainted with its predecessors may be confused on this point. In the former papers I have studied the effect of adding various gases and vapours to active nitrogen after it is formed. In this case, of course, the addition is made by a tributary stream flowing into the stream of nitrogen ufter it has flowed past the place where electric discharge is maintained. In the apparatus, fig. 2, it would flow in at a side tube placed in some such position as M. But the present investigation studies the effect of added substances in assisting the production of active nitrogen. In this case the amount added is much smaller, and the addition is made before the nitrogen is submitted to electric discharge. Some substances have an important and distinct effect in both ways. Thus acetylene is capable of assisting formation of active nitrogen (pure yellow afterglow nitrogen bands) if a trace of it is added before the nitrogen is acted on by the discharge; while, if introduced in larger quantities after the gas has been submitted to discharge, it unites chemically with the active nitrogen, forming hydrocyanic acid; and, from the place where the acetylene flows in onwards, the yellow nitrogen glow is entirely replaced by a violet one showing cyanogen spectrum.

^{† &#}x27;Deutsch. Phys. Gesell. Verh.,' vol. 12, p. 613 (1910); see also vol. 12, p. 291 (1910).

- Sir J. J. Thomson's experiments on positive rays* were made on the luminous discharge at low pressures, with the ions moving under large potential gradients, and thus under conditions approaching somewhat to those used for generating active nitrogen. Thus the information they yield with regard to the loading of electrons by atoms and molecules of various gases is more directly applicable than that obtained by the method used by Franck.
- J. J. Thomson found† that negatively charged atoms of hydrogen, carbon, oxygen, sulphur, and chlorine were present among the rays which had passed through a hole in the cathode. Since such an atom had acquired its momentum in moving up to the cathode, it was necessary to assume that it had been positively charged while doing so, that it had picked up an electron subsequently which neutralised it, and then another which electrified it negatively. Some atoms appeared never to acquire a negative charge under these conditions. These were nitrogen, mercury, helium, argon, and the other rare gases.

It will be observed that, with the exception of mercury, the atoms which promote the formation of active nitrogen are precisely those which can become attached to an electron, while those which do not have this effect are precisely the ones which never become attached to an electron in the canal rays.

I think therefore it will be admitted that we have strong grounds for believing that the effect of certain admixtures in promoting formation of active nitrogen is produced by a loading up of the moving electrons in the discharge. In pure nitrogen the electrons are free. When a slight admixture of some gas containing, e.g., oxygen, sulphur or carbon, is present, atoms of the element introduced, set free in the discharge, attach themselves to the free electrons.

To develop the explanation further, some element of hypothesis is unavoidable. It will be supposed, as in previous papers, that active nitrogen consists of monatomic nitrogen. A nitrogen molecule is separated into atoms by the impact of a negative ion in the discharge. If, however, this ion consists of a free electron it is not so effective in administering the right kind of blow as when it is loaded so as to be of atomic dimensions. Hence the great increase in the production of active nitrogen when atoms of a kind suitable to effect this loading are introduced.

It may be asked, If an ion of atomic dimensions is needed, why do not the

^{*} The title is unfortunate as applied to the particular experiments here quoted, which deal with negatively charged rays.

^{† &#}x27;Roy. Soc. Proc.,' A, vol. 89, p. 10 (1910); see also his 'Rays of Positive Electricity, p. 39, Longmans, 1913.

positive ions of nitrogen, which are present even when the nitrogen is absolutely pure, serve the purpose? The fact that they move in the other direction cannot make the difference.

I think that this objection can be answered without additional hypothesis. The mean free path of an electron is greater than that of a positive ion, on account of its small size. If the positive ion is comparable in radius to the molecules of the gas, the ratio of free paths may be taken as 4 to 1. If, therefore, the electron only acquires its load towards the end of a free path it will have passed over a potential difference four times as great, and therefore have acquired four times the kinetic energy that a positive ion, which of course retains its atomic dimensions throughout, would possess. This possibility of possessing fourfold kinetic energy seems a sufficient explanation of why the negative ions should be so much more capable of producing active nitrogen than the positive ones.

It remains to discuss the exceptional case of mercury, which is moderately efficient in promoting formation of active nitrogen, but which does not take a negative charge in the canal rays. The mercury atom also shows an exceptional behaviour in the canal rays—it occurs with much larger positive electric charges than do other atoms,* the charge being in some cases as much as seven times the electronic charge. Such highly charged positive atoms in the electric field will acquire between collisions the large amount of kinetic energy which we have supposed necessary to administer the necessary shock to a nitrogen molecule. So that this exception may perhaps not unfairly be considered rather confirmatory than otherwise of the theory suggested.

As already mentioned, I have never been able to really reduce the glow to nothing, by any method of purification tried. It is difficult to decide whether this is possible, and even if it did seem to be accomplished in any experiment the doubt would remain whether somewhat different methods of stimulation† would not restore it. In the experiments described the glow was reduced to a point where the addition of 1/30,000 part of a hydrocarbon, such as methane, would distinctly improve it, so that to decide the question experimentally would be very difficult. It seems not inconsistent with the theory suggested that occasionally under favourable circumstances the impact of an unloaded electron might lead to formation of active nitrogen. If so, no purification could reduce the glow to nothing.

The above discussion has purposely been placed in a separate section of the

^{*} J. J. Thomson, loc. cit.

[†] Particularly the electrodeless discharge at low pressures. It is certainly a matter of great difficulty even to appreciably reduce the glow in this case.

paper. If exception is taken to it as too speculative, it is hoped that the experiments of the preceding section will be judged independently.

§ 3. Action of Active Nitrogen on Liquid Metals.

It has been shown* that active nitrogen reacts with metallic vapours, yielding the nitrides. At the same time there is a development of the line spectrum of the metal. No apparent effect is produced when the active gas is passed over clean cold metals or over a film of mercury held on copper.† I now find that if a small quantity of mercury is placed in the bottom of a fairly wide U-tube, and shaken while the active gas passes over it, all luminosity is extinguished, and the mercury becomes foul, clinging to the walls of the vessel, as it does when treated with ozone. If the shaking is discontinued the glow again passes. After having treated the mercury in this way for a short time it is easily proved, chemically, to contain nitride. If water is added ammonia is formed, and can be distilled off and recognised by the Nessler reaction.

It is of interest to notice that when active nitrogen unites in this way with liquid mercury there is no development of the mercury spectrum. This is in contrast to what is found with mercury vapour, which gives the mercury spectrum strongly with active nitrogen. Other melted metals also react with active nitrogen. This was readily demonstrated with fusible metal (bismuth-tin-lead alloy) melting at about 100° C. Metals melting much above this temperature are less easily experimented with, because active nitrogen passes almost instantly into ordinary nitrogen by the catalytic action of hot surfaces. Thus the active nitrogen is destroyed by contact with the heated walls of the glass tube containing the melted metal before getting to the latter. In spite of this difficulty it has been found possible to demonstrate the chemical action upon melted tin and melted lead. As in the case of liquid mercury, the spectrum of the metal is not developed.

§ 4. Experiments with Other Liquids.

These experiments with melted metals naturally suggested trying other liquids.

Since a stream of active nitrogen at low pressure can alone be used, we are limited to liquids of small vapour pressure. The glowing gas was bubbled§

^{*} I, p. 224; V, p. 542.

[†] I, p. 225.

[‡] See III, p. 363.

[§] Bubbling is feasible with a "head" of 1 or 2 cm. of a light liquid. Active nitrogen cannot well be bubbled through molten heavy metals, because the pressure in the discharge tube which this would require would be unfavourable to formation of active nitrogen. Shaking the liquid in the stream of active gas must then be resorted to.

through glycerine in a U-tube without any apparent action. The glow got through quite well.

It was also bubbled through a concentrated solution of stannic chloride. Nothing was seen of the beautiful blue light developed when the vapour of this salt mixes with active nitrogen.

A dilute solution of indigo in concentrated sulphuric acid was slowly decolorised by bubbling active nitrogen through it. The exact nature of the action was not studied further, but the experiment clearly proves that active nitrogen is capable of acting on dissolved substances as well as on vapours and liquid metals.

§ 5. Chemical Action on the Paraffins.

Active nitrogen, it is agreed by all experimenters, acts freely on the majority of carbon compounds, with formation of hydrocyanic acid. Doubts, however, have been expressed as to its having this action on the paraffins.*

1 have re-examined this question as carefully as I could, with the advantage of having specially purified materials at command. In all cases abundant hydrocyanic acid was obtained.

Heptane.—The specimen was one which was specially purified by Sir Edward Thorpe.† Its origin was from Pinus Sabiniana. This was treated with active nitrogen for a few minutes, and an abundant precipitate of prussian blue, enough to colour several litres of water strongly, was obtained. The excess of oil, condensed out along with the hydrocyanic acid, had acquired a strong smell suggestive of nitriles.

Pentane.—The specimen was obtained through the kindness of Dr. A. G. Vernon Harcourt, F.R.S., and had been prepared for use in his standard lamp. It had passed the tests imposed by the Metropolitan gas referees for absence of olefines. This again behaved in just the same way as the heptane had done. The hydrocyanic acid was estimated quantitatively, and the yield was about the same as that formerly obtained; with commercial light petroleum (motor spirit).

Methane.—The first sample was prepared from sodium acetate and soda lime and condensed with liquid air. It was then allowed to evaporate fractionally, the less volatile half of the gas being rejected. About 2 litres was retained for the experiment. After treatment with active nitrogen it yielded hydrocyanic acid equivalent to about 6 c.c. of nitrogen gas.

Two litres of methane prepared from aluminium carbide, and similarly

^{*} Koenig and Elöd, 'Ber. d. Deutsch. Chem. Ges.,' vol. 47, Heft 4, p. 516 (1914).

^{+ &#}x27;Chem. Soc. Proc.,' p. 299 (1879).

¹ V, p. 546.

purified by fractional distillation, gave about the same result as the foregoing.

With methane the cyanogen spectrum is not nearly so conspicuous as with some hydrocarbons; but if the conditions are suitably adjusted, with not too large a feed of methane, it is quite well seen.

§ 6. Summary.

- 1. The past controversy as to whether active nitrogen can be freely obtained from pure nitrogen, or whether a trace of oxygen must be present, is reviewed. It is shown that neither alternative is correct. Perfectly pure nitrogen will not give more than a little active nitrogen. On the other hand, to get a good yield it is not necessary that free oxygen or any oxygen compound should be present, for almost any small admixture of a foreign gas will enormously increase the yield of active nitrogen. The amount of admixture required to produce the best effect is usually of the order of 1/1000 part, but, to quote one case particularly examined, a very distinct effect is produced by adding a 1/30,000 part of methane.
- 2. The view is suggested that the impurity acts by loading the electrons in the discharge, and thus altering the character of their impact with the nitrogen molecules. This view is supported by the fact that gases carrying oxygen, sulphur, chlorine, carbon, and hydrogen are capable of promoting formation of active nitrogen. These are atoms which, according to the investigations of J. J. Thomson and Franck, are capable of attaching themselves to electrons in the discharge. On the other hand, argon, helium, and (of course) nitrogen itself, which are not able to load electrons, do not promote formation of active nitrogen. The case of mercury is at first sight anomalous, but reasons are given which seem to explain the anomaly.
- 3. Active nitrogen shaken with cold liquid mercury unites with it, forming nitride, but no development of mercury spectrum attends the action, as when mercury vapour unites with active nitrogen. Similar results have been obtained with other melted metals.
- 4. Active nitrogen bubbled through a weak solution of indigo in sulphuric acid slowly discharges the blue colour.
- 5. Active nitrogen acts freely on the purest heptane and pentane obtainable, with formation of hydrocyanic acid. On pure methane the action, though perhaps rather less, was still considerable. These experiments do not bear out the view that it is only olefine impurities in the paraffins that can yield hydrocyanic acid.

Some Temperature Refraction Coefficients of Optical Glass.

By Lieut.-Col. J. W. Gifford.

(Communicated by Prof. S. P. Thompson, F.R.S. Received February 6,— Revised March 18, 1915.)

In a previous paper,* the refractive indices of a number of typical samples of glass were given, but the temperature coefficients—although measured—were omitted at the time. The late Sir David Gill having shortly before his death expressed a wish that they should be published, the following paper complies with this desire.

In addition a table is given of the refractive indices of glass meltings since measured, together with an account of an attempt to determine, if only approximately, the influence of atmospheric pressure (barometer changes) on measurements of refractive index generally.

The special methods employed to obtain the indices and to estimate the probable error, as well as the instruments used, are the same,† except in the case of Schott's Fluor Crown. In this case, the melting being a small one, only one prism was cut, and the limit of uniformity in its production has, therefore, not been ascertained; it may, however, be noted in this connection that its temperature refraction coefficient is a minus quantity as with quartz and fluorite. In no other glass melting has this been found by the author, all others having the plus sign, that is, the refractive index in air rises with the temperature.

In order to determine the change in the apparent refractive index due to the varying barometric pressure, a number of experiments were made in which on different days the refractive indices were compared, the temperature so far as possible being the same. It was pointed out to me by Prof. Schuster that these experiments indicated that far the greatest part of the change was due to alteration of the refraction in air.

Tables of the temperature refraction coefficients of all the glasses and of the refractive indices of those meltings not previously given follow.

It should be noted that the numbers indicating the "probable error" include the actual differences in the refractive indices of different specimens of glass from the same melting and the accidental errors of the determination of the index of each. The former, as pointed out in my previous paper, is much the larger of the two. The refractive indices are referred to air. The

^{* &#}x27;Roy. Soc. Proc.,' vol. 87, p. 189 (1912).

^{† &#}x27;Roy. Soc. Proc.,' vol. 70, p. 329 (1902); and 'Monthly Notices R.A.S.,' vol. 69, p. 118 (1908).

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Note. - Indices in brackets have been interpolated.

temperature coefficients indicate the changes of the index due to a rise of 1° C., the normal temperature being 15° C. In order to reduce these indices to vacuo, corrections have to be applied which are easily calculated. Approximately the correction is minus 10 in the last decimal place, so that "Silicate Crown (S. 7181)" would have a zero coefficient for the refractive index referred to vacuo.

Table of Temperature Refraction Coefficients ($\lambda = 5270$) for 1° C.

Type.	•	
0,6781	Fluor Crown (8. 8897)	~0·0000035 *
0,2188	Borosilicate Crown (8. 6115	0 .0000021
411	" " (C. 557)	0 .0000019
0,144	" " " (8. 5077)	0.0000080
0,8882	" " " (S. 5028	0 .0000102
0,144	" " " (S. 6141	0 0000014
8790	,, ,,	0.0000040
0,8890	,, ,, (8. 3581)	0.0000020
0,3512	,, ,,(S. 6107)	0 ·0000018
0,3453	,, ,, (S. 4812)	0.0000015
0,2118	Crown of lowest μ_D (S. 3113)	0.0000036
0,188	Silicate Crown (S. 7181)	0.0000010
0,3655	Telescope Crown (S. 3418)	0 .0000007
0,8551	Zinco-silicate Crown (S. 4705)	
0,227	Barium Silicate Crown (8. 7714	0 .0000049
0,211	Densest Barium Silicate Crown (S. 4962)	0 0000012
4087	Baryta Light Flint (M. 4087)	
0,8439	Telescope Light Flint (S. 8204)	
0,826	Baryta Light Flint (S. 4677)	
0,3489	Telescope Light Flint (S. 4805)	0 .0000028
0,2071	Dense Barium Crown (S. 4674)	\$0.0000004
4078	Heavy Barium Crown (M. 5201)	0.0000038
0,8439	Telescope Flint (8. 5992)	
0,3961	Densest Baryta Crown (8, 4704)	0 0000058
0,3388	Borosilicate Flint (S. 3338)	
0,527	Baryta Light Flint (8, 3187)	
0,864	Borosilicate Flint (S. 8198)	0.0000105
0,578	Baryta Light Flint (S. 5042)	0 .0000035
0,364	Borosilicate Flint (S. 0864)	
0,154	Ordinary Light Flint (8, 3831)	
8885	Light Flint (M. 6812)	
0,748	Baryta Light Flint (M. 4870)	
384	Dense Flint (C. 629)	0.0000070
0,118	" " " (S. 5408)	0 .0000022

The temperature refraction coefficients for—

Quartz (ordinary ray)...... = -0 '0000052 Fluorite -0 '0000102 The Effects of Different Gases on the Electron Emission from Glowing Solids.

By Frank Horton, Sc.D., Professor of Physics in the University of London.

(Communicated by Sir J. J. Thomson, O.M., F.R.S. Received March 4, 1915.)

The original theory of the origin of the electron emission from glowing solids, which is based on the electron theory of metallic conduction, has recently been subjected to criticism on account of the manner in which the emission can be reduced by continually removing impurities from the discharge tube. The critics maintain that the emission occurs as a result of chemical action between the hot cathode and the surrounding gas, or between the constituents of the cathode itself. In a recent paper* the author has summarised the evidence in favour of this latter view, and has described experiments which show that the results which it leads us to expect do not always occur. In particular it has been shown that the chemical action theory of the origin of the activity of a Wehnelt cathode, as propounded by Fredenhagen† and by Gehrts, tcannot be accepted. The experiments described in the present paper were designed to test further the theory that the electron emission is due to chemical action. The experiments consisted in studying the ionisation produced by Nernst filaments heated in various gases, of different chemical affinities for the material of the cathode. apparatus and method of experiment were similar to those described in the paper already referred to. The filament was heated by an alternating current from a transformer, and its temperature was determined by means of a specially standardised Féry optical pyrometer which was kindly lent to me by Prof. T. Mather, of the City and Guilds Engineering College, London. The anode consisted of two parallel platinum plates, fixed in the discharge tube at equal distances on opposite sides of the filament, and connected together outside the apparatus. The potential difference applied to the ends of the filament was measured by a Siemens alternating voltmeter, which was used in series with a resistance of equal magnitude, the total resistance in parallel with the filament being 4572 ohms. The junction of the voltmeter and series resistance was connected to earth, and thus the mid-point of

^{*} F. Horton, 'Phil. Trans.,' A, vol. 214, p. 277 (1914).

[†] K. Fredenhagen, 'Ber. K. Sächs. Ges. Wiss.,' Leipzig, vol. 65, p. 42 (1913).

¹ A. Gehrts, 'Ber. d. Deutsch. Phys. Ges.,' p. 1047 (1913).

[§] The author is indebted to the Government Grant Committee of the Royal Society for the means of purchasing some of the apparatus used in these experiments.

the glowing filament was kept at zero potential. The platinum plates forming the anode were connected through a delicate galvanometer to the positive pole of a high potential battery, the negative pole of which was earthed. A diagrammatic view of the arrangements is given in fig. 1, in which for simplicity the discharge tube is not shown. The filaments experimented

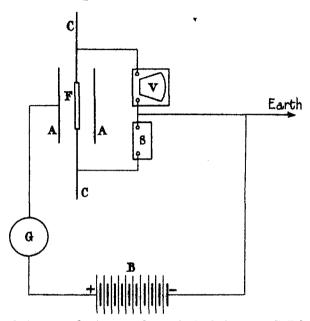


Fig. I.—A, A, platinum anodes (connected together); B, battery; C, C, heating current leads; F, Nernst filament; G, galvanometer; V, voltmeter; S, series resistance.

with were all of the same type and were intended for use on a 100-volt alternating circuit. The thermionic currents in air under similar conditions varied slightly for different filaments, but in every case the currents measured after heating for some time were remarkably constant. In this respect the electron emission from a Nernst filament is very different from that obtained with a metal cathode, which usually decreases continuously with time. Measurements of the thermionic currents in air, nitrogen, oxygen, and hydrogen were made. In each case the variation of the current with the pressure of the gas under a constant applied potential difference was observed, and also the variation of the current with the potential difference with a constant gas pressure in the discharge tube. The observations were usually made with the filament at a temperature of 1525° C., but measurements were also made at other temperatures.

A difficulty in making comparisons of the thermionic currents in different gases, and at different pressures in the same gas, arises from the fact that, in

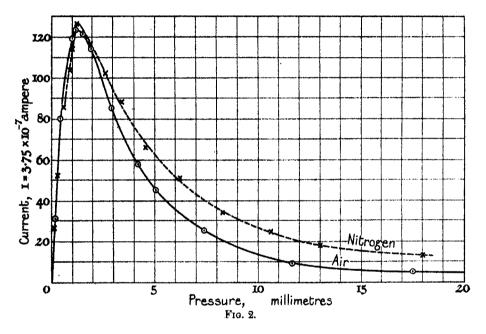
order to maintain the filament at a constant temperature, the heating current has to be altered at each change in the nature or density of the surrounding As the thermionic current is usually unsaturated, an alteration of the potential difference between the ends of the filament causes an alteration in the current measured by the galvanometer. For this reason the comparisons were generally made with a potential difference of 210 volts applied between the centre of the filament and the platinum anodes, this large potential difference being used so as to minimise the effect of the variations in the heating circuit. Another difficulty occurred in the measurement of the temperature, for it was found that at very low pressures (less than about 0.15 mm.) the luminosity of the filament fell off, although the heating current was maintained steady. It is thus possible that the thermionic currents measured at these low pressures are larger than they should be, on account of the temperature of the filament being greater than the value obtained from the reading of the optical pyrometer; but I do not think this introduces a serious error, for the pyrometer measures the temperature by the intensity of the red rays only, and it was found that, if the heating current were kept constant, the intensity of the red rays hardly altered as the gas pressure was reduced from about 0.1 mm., although the general luminosity of the filament decreased perceptibly. A Nernst filament seems to require the presence of oxygen in order to emit a brilliant white light at high temperatures, for it was noticed that the luminosity was less, and that the filament appeared redder, when heated in nitrogen or hydrogen than when heated in the presence of oxygen to the same temperature as measured by the pyrometer.

In comparing the thermionic currents in air with those under similar circumstances in another gas, a series of observations in air was usually taken first. The filament was fitted into the apparatus and left glowing for some time in air at the highest pressure to be used. During this period the air in the apparatus was dried by the large phosphorus pentoxide drying tube connected to the discharge bulb, and the measured thermionic current gradually attained a steady value. Even with a new filament, the thermionic current became constant after a few hours' heating. The pressure of the air in the apparatus was then gradually reduced, the temperature and applied potential difference being kept constant, and observations of the thermionic current at different pressures were taken. The vacuum was finally made as complete as possible by means of charcoal cooled in liquid air, and then the other gas was gradually let into the apparatus, through two stopcocks, from a large glass flask, where it had been stored for many hours over phosphorus pentoxide. Several filaments were used in the course of these experiments, and, as these gave slightly different thermionic currents under similar

conditions, it was necessary to make a series of experiments in air in connection with each series of observations in another gas. The results will therefore all be given in the form of a comparison of the ionisation produced in air with that produced in the second gas.

I. The Ionisation in Nitrogen.

The current-pressure curves for air and for nitrogen are shown in fig. 2. The filament was at a constant temperature of 1525° C. throughout the observations, and a potential difference of 212 volts was applied across the tube. It will be seen that in both cases the maximum thermionic current

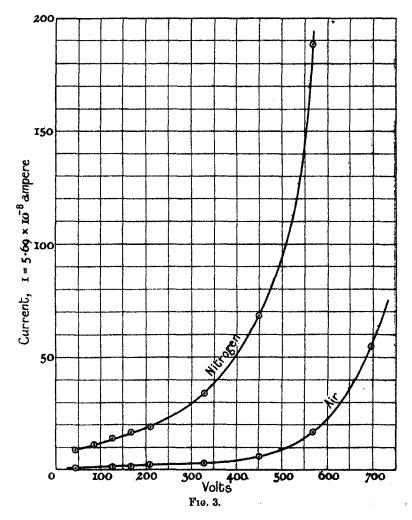


was obtained at about 1.3 mm. pressure, and that at pressures below this the current was practically the same in the two gases, while at higher pressures the current in nitrogen was rather greater than that in air at the same pressure. This is also shown by the current-E.M.F. curves at different pressures in the two gases. At very low pressures the curves were nearly identical, but at pressures of several millimetres the currents in nitrogen were always greater than those under similar conditions in air. Fig. 3 shows these curves for the two gases at 48 mm. pressure.

Both with air and with nitrogen the current-E.M.F. curves showed the usual characteristics, approximate saturation at very low pressures, and at pressures approaching atmospheric, with evidence of considerable ionisation

by collisions at intermediate pressures, as, for instance, is shown by the curves in fig. 3.

It should be mentioned that all the currents measured with the particular filament used in this series of experiments were rather larger than those



usually obtained, probably owing to some slight difference of composition of the filament.

II. The Ionisation in Oxygen.

The current-pressure curves obtained in oxygen were practically identical with those obtained with the same filament in air. The pressure of maximum thermionic current was found to be about 1 mm.—a little lower than that

measured with the filament used in the experiments with nitrogen. The current-E.M.F. curves were also very similar. The equality of the currents measured at low pressures in the two gases may be judged from the following Table, which gives the galvanometer deflections for different applied potential differences, in air at 0.161 mm. pressure and in oxygen at 0.148 mm. pressure, the temperature of the filament in both cases being 1525° C.:—

Potential difference (volta).	Thermionic currents: $1 = 1.40 \times 10^{-8}$ ampère	
rotential difference (votes).	Air.	Oxygen.
48	48	-51
86	79	84
129	102	118
172	129	146
258	189	199
844	245	255
480	810	816

In taking the observations for a current-E.M.F. curve in any gas it was usually found that the currents measured with increasing electromotive forces were in each case slightly less than the currents measured under the same potential differences with decreasing electromotive forces. This was the case during the observations recorded in the above Table, and the numbers given for the currents are the means of the "increasing E.M.F." and the "decreasing E.M.F." values.

III. The Ionisation in Hydrogen.

The effect of hydrogen on the discharge of negative electricity from a glowing solid was first investigated by H. A. Wilson,* who experimented with a hot platinum wire and found that hydrogen produced a very large increase in the thermionic current, which, at low pressures, was nearly proportional to the pressure of the hydrogen. From these results Wilson was led to the conclusion that the negative emission ordinarily observed from a platinum wire at a high temperature in air, or in a vacuum, was probably due to traces of hydrogen in the wire, and he showed that the thermionic current may be reduced to 1/250,000 of its ordinary value by taking precautions to remove such traces. Further experiments,† however, convinced Prof. Wilson that the electron emission from glowing platinum is not entirely due to traces of hydrogen, but that the presence of this gas in the surface layers of the platinum assists the escape of electrons from the metal by diminishing the

^{*} H. A. Wilson, 'Phil. Trans.,' A, vol. 202, p. 243 (1903).

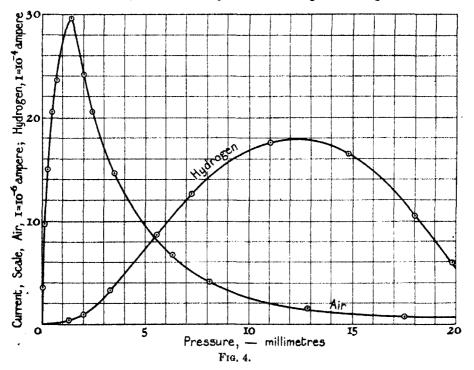
[†] H. A. Wilson, 'Phil. Trans.,' A, vol. 208, p. 247 (1908).

work which an electron has to do in passing through the surface. Other experimenters have, nevertheless, used the fact that the thermionic current can be increased by the presence of hydrogen, as an argument in favour of the view that the electron emission from glowing solids is purely the result of chemical action between the cathode and impurities present in it, or gases surrounding it—that the electrons are liberated by chemical action and are not simply escaping from the cathode at the high temperature.

The main object of the experiments recorded in the present paper was to investigate the electron emission from a Nernst filament in hydrogen, and to compare it with the emission in other gases. Many more experiments were, therefore, made in hydrogen than in oxygen or nitrogen, and the thermionic currents from several filaments in this gas, under different conditions, were very thoroughly investigated. It is clear that the possibilities of chemical action with a Nernst filament (consisting of a mixture of oxides) at a high temperature are much greater when the gas in the apparatus is hydrogen than when oxygen, nitrogen, or air are used. If the emission of electrons is due to chemical action, it would seem reasonable to expect a much larger emission from the filament in hydrogen than under similar conditions in other gases. But the results of the experiments given below show that the emission in hydrogen is not greater than the emission in air, although at certain pressures the thermionic current is enormously increased by the ionisation of the hydrogen molecules by collisions. The increase in the current due to this cause in hydrogen is very much greater than the corresponding increase in air, oxygen, or nitrogen.

The curves given in fig. 4 show the alteration with gas pressure of the thermionic current from a filament at 1525° C, in air and in hydrogen, the currents measured in the latter gas being plotted to one-hundredth the scale of those in air. It will be seen that the pressure of maximum conductivity in hydrogen is about 8.5 times the pressure of maximum conductivity in air. On the theory of ionisation by collisions the pressure at which the current attains a maximum value is proportional to the electric force. A series of observations with the filament at 1525° C, in air showed that the pressure of maximum thermionic current was roughly proportional to the potential difference applied from the cells for voltages of 200 and 250. The voltage applied from the cells is, however, only a measure of the potential difference between the centre of the filament and the anodes. The potential at other points of the filament is different from that at the centre owing to the fall of potential along the heating circuit. In hydrogen the heating current required to maintain a temperature of 1525° C. is much greater than in air, and it increases considerably as the pressure of the hydrogen is increased.

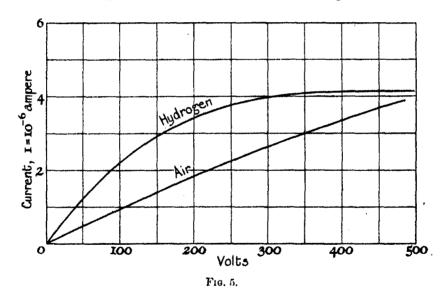
electric field due to the heating current is therefore by no means constant during a series of experiments at different gas pressures, and it is very different in hydrogen at 12 mm. pressure and in air at 1.4 mm. pressure. It is thus probable that the pressure of maximum thermionic current in hydrogen as shown in the curve is considerably higher than it would be if the electric field were the same as in the case of air. It follows from the theory of ionisation by collisions that with a given uniform field the pressure of maximum current in hydrogen is about three times the corresponding pressure in air, oxygen, or nitrogen. In the present experiments the



electric field is not uniform, and it alters when the heating current is adjusted at each change of pressure, so that we should not expect this ratio to be obtained, although the general form of the curves indicates that the variations in the thermionic current with gas pressure are due to ionisation by collisions. Several series of experiments made with different filaments in hydrogen and in air gave pressures of maximum conductivity in the former gas ranging from 8.0 to 9.5 times the pressure of maximum conductivity in air. To give some idea of the manner in which the field due to the heating current varied it may be mentioned that, with the filament at 1525° C., and with air in the apparatus, the potential difference

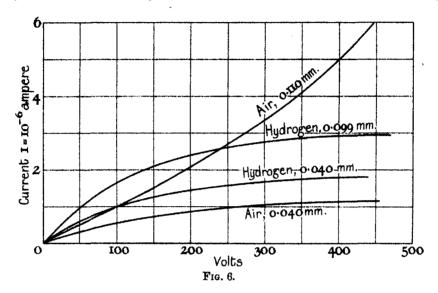
between the ends of the filament ranged from 74 to 66 volts as the pressure was reduced from about 40 mm. to zero; while in hydrogen the corresponding alteration was from 128 to 66 volts.

In order to compare the electron emissions in air and in hydrogen it is necessary to prevent, as far as possible, the original emission from being altogether swamped by the new ions formed by collisions. It was not possible to prevent ionisation by collisions altogether, for it was necessary to have some gas present in the discharge tube, and it was found that the field due to the heating current alone was sufficient to cause this ionisation; but the effects of ionisation by collisions are not large if the experiments are made at low pressures—at pressures well below those of the maxima shown in the curves of fig. 4. A series of observations of the thermionic currents in air and in hydrogen with various applied potential differences, and at pressures up to 0.2 mm., was therefore made. Fig. 5 shows current-



E.M.F. curves for air and for hydrogen at 0.17 mm, pressure, the temperature of the filament being 1525° C. in both cases. From these curves it will be seen that the thermionic current is nearly the same in the two gases. With 400 volts the current in hydrogen appears to be saturated, whereas that in air is approximately obeying Ohm's law. A similar result is shown in fig. 6 for hydrogen at 0.099 mm, and for air at 0.110 mm. The experiments for the curves in fig. 6 were made with a different apparatus from that used in obtaining the results of fig. 5, the distance apart of the electrodes being rather greater. Fig. 6 also contains

curves for hydrogen and for air at 0.040 mm. pressure, under which conditions the currents in the two gases are still more nearly equal. At this lower pressure the effects of gas ionisation are no doubt smaller, for not only are fewer collisions possible, but also the electric field is more nearly



the same in the two gases, as the heating currents required to maintain the same temperature in the filament are not very different. These curves, and others which I have obtained, show that at low pressures saturation is more easily attained in hydrogen than in air, oxygen, or nitrogen; a result which is accounted for by the fact that the mean free path of the ion in hydrogen is greater than it is in air, oxygen, or nitrogen, and so becomes comparable with the distance between the electrodes at a higher pressure than in the case of these other gases. The curves clearly indicate that if ionisation by collisions could be completely eliminated, the electron emission from the filament would be found to be the same in hydrogen as it is in air.

IV. A Comparison of the Electron Emission from Lime Heated on a Nernst Filament in Air and in Hydrogen.

In the course of an earlier research* the author found that the thermionic current from a lime-covered platinum strip heated in pure helium at about 3 mm. pressure was enormously increased if a small quantity of hydrogen was allowed to enter the discharge tube. Since the amount of hydrogen admitted was very small, it is probable that the increased current obtained is due to an

^{*} F. Horton, 'Phil. Trans.,' A, vol. 207, p. 149 (1907).

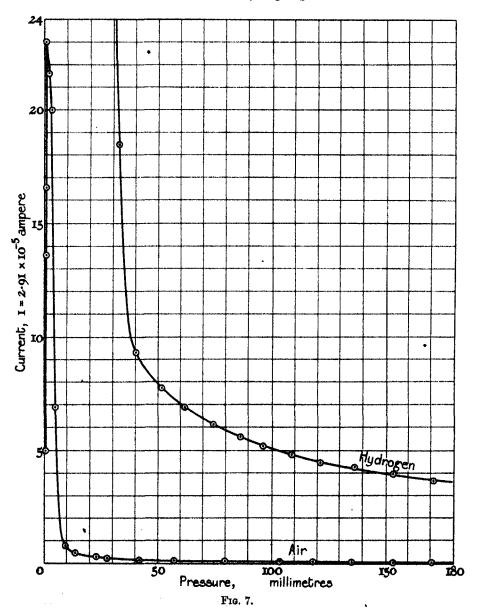
actual increase in the emission from the cathode, and is not merely the result of ionisation of the hydrogen atoms by collisions. It was also found that the thermionic current in pure hydrogen at 0.01 mm. pressure was enormously greater than the current measured in air at the same pressure. Recently Fredenhagen* has attempted to explain this effect from the point of view of the chemical action theory of the emission of electrons from solids at high temperatures, by supposing that the hydrogen combines with the oxygen of the lime, and possibly also with the calcium, and that electrons are emitted as a result of these chemical actions. An obvious objection to this explanation is that it involves the rapid disappearance of the oxide layer, and consequently the cessation of the activity of the cathode—results which do not occur in practice. There is also the objection that, so far as the author is aware, there is no evidence that the chemical actions mentioned give rise to an electron emission.

The experiments described in the present paper suggested that the increased emission from a lime-covered platinum cathode in hydrogen might be due to the effect of the hydrogen on the emission from the platinum supporting the lime, so that if the lime were heated without the platinum support, its electron emission in hydrogen might perhaps be not very different from that in air. In order to test this, a Nernst filament which had been found to give equal thermionic currents in air and in hydrogen at low pressures was covered with lime and was again tested in these gases. results of these tests will be seen from the curves given below. Fig. 7 shows the current-pressure curves at 1525° C. in air and in hydrogen. It will be seen that at 100 mm, pressure the thermionic current in hydrogen was about 55 times the current in air, but the shape of the curve indicates that ionisation by collisions is already occurring at this pressure in hydrogen, whereas it is producing no noticeable effect in air; moreover the potential difference between the ends of the filament at 100 mm, pressure was 136 volts in hydrogen and only 79 volts in air. The alteration of the thermionic currents with pressure, at pressures below about 1 mm., is shown in fig. 8. Ionisation by collisions takes place throughout this region of pressure, especially when a high potential difference is applied across the tube. Both with air and with hydrogen there was a luminous discharge throughout the series of observations represented in fig. 8. At high pressures the discharge with a potential difference of 206 volts (as in the curves of fig. 7) was not luminous, but the luminosity appeared on reducing the pressure to about 33 mm. with hydrogen, and to about 4 mm. with air.

In comparing these results in the two gases it must be borne in mind that

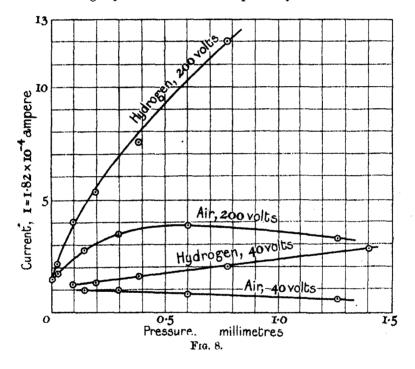
^{*} K. Fredenhagen, 'Physik. Zeitschr.,' vol. 15, p. 19 (1914).

apart from the effects of ionisation by collisions, there are two things which tend to make the currents measured in hydrogen greater than those measured



in air. One of these is the greater potential difference between the ends of the filament, due to the greater heating current required in hydrogen; the other is the fact that the luminosity of the filament in hydrogen is less than

it is in air. With the optical pyrometer, only the red light is used to measure the temperature, and I do not think that much error is made in adjusting the temperature with a low pressure of air or of hydrogen in the apparatus; but at high pressures, where the difference of luminosity in the two gases is more marked, it is not unlikely that a higher temperature of the filament is required in hydrogen to give the same intensity of red light as is obtained with the filament at 1525° C. in air. It is probably for these reasons that the ratio of the thermionic currents in the two gases was found to increase at high pressures. At atmospheric pressure the current in

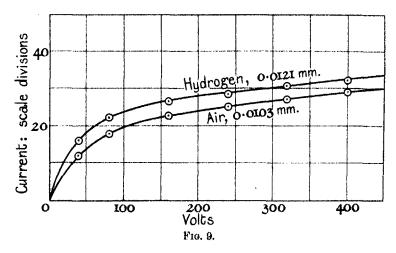


hydrogen was about 400 times as large as the current measured in air under the same applied potential difference and at the same temperature as measured by the pyrometer. Unfortunately, no other method of temperature measurement could be employed, for it was desired to have no metal in contact with the lime. These experiments at atmospheric pressure can be compared with those of Martyn,* who found that the thermionic current from a lime-covered platinum wire at 1600° C. in hydrogen at atmospheric pressure was 20,000 times the current in air under similar conditions. In Martyn's experiment there was no uncertainty in the temperature adjustment, which

^{*} G. H. Martyn, 'Phil. Mag.,' VI, vol. 14, p. 306 (1907).

was performed by measuring the resistance of the platinum wire. It is therefore obvious that hydrogen increases the thermionic current from a lime-covered platinum cathode to a much greater extent than it does the current from a lime-covered Nernst filament.

That the electron emission from lime is practically the same in air and in hydrogen is perhaps best shown (as in the case of the Nernst filament alone) by current-E.M.F. curves obtained at low pressures. Two such curves are given in fig. 9, the lower one being for air at 0.0103 mm. pressure, the upper one for hydrogen at 0.0121 mm. pressure. During both sets of observations the gas in the discharge tube was very faintly luminous. The luminosity



was not sufficient to enable the spectra of the gases to be examined, but this was done before reducing the pressure in each case; the air showed no sign of the hydrogen lines, and the spectrum of the hydrogen showed that the gas was pure.

To illustrate the striking difference between these results and the effect of hydrogen on the thermionic current from a lime-covered platinum strip, an experiment described in an earlier paper* may be quoted. The thermionic current from a lime-covered platinum cathode was measured in oxygen gas at 0.002 mm. pressure. This gas was pumped out and hydrogen was let into the apparatus, which was then pumped down to the same pressure as before. On warming up the cathode the thermionic current was at first only slightly greater than its previous value, but it rapidly increased until in a few minutes it was over 10,000 times as great as it had been in oxygen at the same temperature (740° C.). In view of the results of the experiments described

^{*} F. Horton, 'Phil. Trans.,' A, vol. 207, p. 149 (1907).

in the present paper, this increase in the thermionic current is probably entirely due to the effect of the hydrogen upon the platinum. In the first observation, in oxygen, the platinum was quite free from hydrogen. It had been boiled for a long time in strong nitric acid before being covered with lime, and the cathode had been heated in oxygen at a considerable pressure for hours before the final readings at 0.002 mm. were taken. When hydrogen is let into the apparatus it is only very slowly absorbed by the platinum when that is cold, but as the temperature is raised the absorption rapidly increases. This probably accounts for the increasing thermionic current which was observed in the experiment.

Summary and Conclusion.

The experiments described have shown that the emission of electrons from a glowing Nernst filament is independent of the nature of the gas in the discharge tube, at least for the gases air, oxygen, nitrogen, and hydrogen, and that the same may be said of the electron emission from lime. At low pressures the thermionic current from a given cathode under definite conditions is practically identical in all four gases. At higher pressures the thermionic currents under similar conditions vary, but an increased thermionic current does not necessarily mean an increased electron emission from the cathode; the large currents which are obtained at certain gas pressures, particularly with hydrogen, are the result of ionisation of the gas molecules by collisions. Oxygen and hydrogen differ very widely in their chemical affinities for the material of an oxide cathode, so that the equality of the electron emission in these two gases is evidence that the electrons are not produced by chemical action between the cathode and the surrounding gas.

In the case of a platinum cathode, hydrogen seems to produce a genuine increased emission, which appears to be brought about by the absorption of the gas by the platinum. This result was first obtained by H. A. Wilson,* who, by means of a careful investigation of the connection between the thermionic current and the gas pressure, was able to establish the fact that the hydrogen dissolves in the platinum and does not, under ordinary circumstances, combine with it to form a compound. It is improbable, therefore, that the increased emission from platinum produced by hydrogen is due to chemical action. The exact manner in which the hydrogen acts is at present unknown, but Wilson has shown that the experimental results can be explained on the supposition that the hydrogen atoms in the surface layers

^{*} H. A. Wilson, 'Phil. Trans.,' A, vol. 208, p. 247 (1908).

of the platinum are positively charged and have the effect of lessening the work which an electron must do in order to escape from the metal. With a substance like lime or the oxides of a Nernst filament, by which the hydrogen is not absorbed, the electron emission is unaltered by the presence of this gas.

On the Corpuscular Radiation Liberated in Vapours by Homogeneous X-radiation.

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(Communicated by Prof. O. W. Richardson, F.R.S. Received March 22, 1915.)

It is recognised as a result of numerous independent experiments* that ionisation by X-rays is the result of corpuscular radiation liberated by the X-rays. In a recent paper† it was shown by the author that, in the case of carbon and oxygen compounds, the corpuscular radiation liberated by a beam of X-radiation was an "atomic" phenomenon, i.e. that the number of corpuscles given out by an atom of carbon or oxygen in a beam of X-rays is the same whether the atom is in combination or not. The resulting ionisation is not, however, "atomic," the ionisation produced in different gases or vapours by a given amount of corpuscular radiation being dependent on the nature of the gas or vapour:

In the present paper an attempt has been made to test whether this "atomic" law holds good for other elements of higher atomic weight. These, giving much larger ionisations than the lighter elements, also allow of greater accuracy in the observations, although as the absorption is correspondingly increased, large absorption corrections are rendered necessary in some cases.

As in the former experiments, the gases or vapours were subjected to a beam of homogeneous (copper) radiation, the ionisation chamber being a cylinder with aluminium ends, and containing an axial electrode connected with an electroscope. The rate of leak due to the ionisation current was compared with that of a standard electroscope containing air, and after each

^{*} Barkla and Simons, 'Phil. Mag.,' February, 1912; C. T. R. Wilson, 'Roy. Soc. Proc.,' June, 1912; Barkla and Philpot, 'Phil. Mag.,' June, 1913.

† 'Phil. Mag.,' January, 1914.

experiment the cylindrical chamber was filled with air, so that the fonisation in air produced by the same beam of X-rays could also be measured.

The effect of corpuscular radiation from the ends of the chamber was reduced to a very small amount by lining the chamber with pure filter paper: it was measured by determining the ionisation produced when the chamber was filled with hydrogen. The ionisation with hydrogen filling the chamber is due entirely to the corpuscles emitted by the ends, and by deducting this amount of corpuscular radiation from that produced in any gas or vapour, the true value for the corpuscular radiation liberated in the gas by the X-rays is obtained. The value of this method in eliminating insulation leaks, if there are any, has been referred to in the previous paper.

In order to obtain the corpuscular radiation in a gas corresponding with a given amount of ionisation observed, it is necessary to know the ratio of the ionisation produced in the gas to that produced in air by equal quantities of corpuscles liberated (and completely absorbed) in each. This ratio, called the "corpuscular factor" in the previous paper, was determined by using a short, wide chamber through which the homogeneous radiation from tin Inside the chamber, both back and front, was a reversible slide carrying a sheet of fine bristol-board coated on one side with gold leaf. These sheets could be mounted so as to allow the corpuscular radiation from the gold to enter the gas in the chamber, or, by reversing the sheets so that the gold faced outwards, the corpuscles were prevented from entering the gas. The intensity of the X-ray beam in the gas was the same in either case, having passed through the same layers of material, so that the ionisation due to absorption by the gas itself was unaltered. The difference between the ionisations in the two types of experiment was thus due to the liberation of a definite quantity of corpuscular radiation in the gas. A similar pair of experiments, using air, enabled the corresponding quantity to be obtained for air, and thus the required ratio could be found. A small correction for absorption is necessary in this type of experiment also; the method of correcting is given later (p. 343).

The substances chosen for experiment were selected mainly on account of their suitability to the particular methods and apparatus employed, but in one or two cases special reasons were also present in making the selection. The experiments of Owen* and of Crowther† on CO₂ did not agree with the results obtained by Barkla and Philpot,‡ and it was considered desirable to re-determine the ionisation in CO₂ and also its corpuscular factor, as a check

^{*} Owen, 'Roy. Soc. Proc.,' May, 1912.

[†] Crowther, 'Camb. Phil. Soc. Proc.,' February, 1909.

^{‡ &#}x27;Phil. Mag.,' June, 1913.

on the results obtained for the atomic corpuscular radiations of carbon and oxygen in the previous paper. Preliminary experiments agreed with the results obtained by Crowther and by Owen, but, on testing with silver nitrate, a minute trace of hydrochloric acid was detected in the final washing tower through which the CO₂ was passed. When further precautions to remove all trace of HCl were taken, so that a tube of silver nitrate solution through which the gas bubbled remained quite clear, the value was reduced to that obtained by Barkla and Philpot and agrees exactly with the atomic results already obtained.

The compounds of chlorine which were used give three different numbers of chlorine atoms in a molecule, and hence form a fair test of the atomic nature of the phenomenon under investigation. Carbon disulphide was used as a convenient sulphur compound in order to obtain a value for sulphur, so as to fill up to a certain extent the somewhat considerable gap between oxygen and chlorine.

In working with the different substances certain modifications of detail were made in the experiments according to the nature of the substance used. With the vapours whose saturation vapour-pressure was less than atmospheric, a mixture of hydrogen and the vapour was used, the mixture being passed through a long spiral surrounded by ice, so that the vapour was saturated at 0° C. Hydrochloric acid and ammonia were each used at atmospheric pressure, as were also nitrous oxide and carbon dioxide.

In the case of ammonia, and to a lesser degree with hydrochloric acid, insulation difficulties were met with, vulcanite proving quite useless even if the chamber was dried with air over P_2O_5 . The difficulty was, however, completely overcome by covering the vulcanite with paraffin wax, the insulation leak being practically zero when this was used.

In order to obtain the ratio of the amounts of corpuscular radiation liberated in equal lengths of the gas in question and of air, by X-ray beams of equal intensity, the following method was used:—Indicating the intensity of the beam by I, the ionisation per centimetre in any gas is AkI, where A represents the corpuscular radiation liberated in the gas per centimetre by a beam of "unit" intensity and k is the corpuscular factor for the gas. The coefficient of absorption in the gas being λ per cm., I at any distance x cm. from the incident end of the chamber will be $=I_0e^{-\lambda x}$, I_0 being the intensity of the incident beam. The ionisation in the chamber, after deducting the small ionisation due to corpuscular radiation from the ends, is thus

$$\int_0^l \mathbf{A}k\mathbf{I} \, dx = \int_0^l \mathbf{A}k\mathbf{I}_0 e^{-\lambda x} \, dx = \frac{\mathbf{A}k\mathbf{I}_0}{\lambda} (1 - e^{-\lambda l}).$$

For two gases (one air) the ionisation ratio observed (called R) is thus

$$R = \frac{A_1}{A_0} k_1 \frac{(1 - e^{-\lambda_1 l}) \lambda_0}{(1 - e^{-\lambda_0 l}) \lambda_1}.$$

The quantity A_1/A_0 is the ratio required, and is evidently given by

$$\begin{split} \frac{\mathbf{A}_1}{\mathbf{A}_0} &= \mathbf{R} \frac{(1 - e^{-\lambda_0 l}) \, \lambda_1}{(1 - e^{-\lambda_1 l}) \, \lambda_0} \frac{1}{k_1} \\ &= \frac{\mathbf{R}}{k_1} \frac{1 - \frac{1}{2} \, \lambda_0 l}{1 - \frac{1}{2} \, \lambda_1 l}, \text{ if } \lambda_1 \text{ and } \lambda_0 \text{ are small.} \end{split}$$

For most of the substances used, λ is not known, but from the work of Barkla and Simons and others, to which reference has already been made, it may be deduced that λ is proportional to A (see p. 343). As a first approximation, λ_1/λ_0 can be taken as equal to R and an approximate value of A_1/A_0 calculated. This value will be too low, but can be used to get a better value of λ_1/λ_0 , and hence by successive approximations the value of A_1/A_0 can be obtained to a close degree of accuracy.

In the rectangular chamber used for determining the corpuscular factor, the ionisation with the gold surfaces inwards would be

$$\frac{\mathbf{A}k\mathbf{I}_0}{\lambda'}(1-e^{-\lambda'l})+c_1\mathbf{I}_0k+c_2\mathbf{I}_0e^{-\lambda'l}k,$$

 λ' being the linear absorption coefficient for tin radiation, c_1 the corpuscular radiation emitted at the first surface for a beam of unit intensity, and c_2 the corresponding quantity for the second surface. With the gold surfaces facing outwards, the ionisation would be

$$\frac{\mathbf{A}k\mathbf{I}_0}{\lambda'}(1-e^{-\lambda''})-c_3\mathbf{I}_0k+c_4\mathbf{I}_0e^{-\lambda''}k,$$

 c_3 and c_4 being the corpuscular radiations from the cardboard surfaces for a beam of unit intensity: these quantities are very small indeed. The difference in the ionisation in the two cases is

$$k \{ (c_1-c_3) I_0 + (c_2-c_4) I_0 e^{-\lambda' t} \}.$$

The ratio of the differences for a gas or gaseous mixture and for air is thus

$$\frac{k_1}{1} \frac{\left\{ (c_1 - c_3) + (c_2 - c_4) e^{-\lambda_1' l} \right\}}{\left\{ (c_1 - c_3) + (c_2 - c_4) e^{-\lambda_0' l} \right\}}.$$

This reduces to

$$k_1 \left\{ 1 + \left(\frac{c_2 - c_4}{c_1 - c_8} \right) (e^{-\lambda_1 l} - e^{-\lambda_0 l}) \right\}$$
 ,

or, neglecting c_3 and c_4 , and taking $\lambda_1'l$ and $\lambda_0'l$ small, the observed ratio is

$$k_1\left\{1-\frac{c_9}{c_1}(\lambda_1'-\lambda_0')l\right\}.$$

The observed corpuscular factor being indicated by k_1' , the true corpuscular factor is

$$k_1 = k_1' \left\{ 1 + \frac{c_2}{c_1} (\lambda_1' - \lambda_0') l \right\}.$$

The ratio c_2/c_1 has been determined by Philpot* and is equal to 0.90. The value of λ_0' (for air) is known, and the value of λ' for the other substances was calculated as described above.

In one or two cases, these corrections were large, as will be seen on comparing Columns V and VI in Table I, but there is no reason why they should not be reasonably accurate, and the corrected values of the corpuscular radiations liberated correspondingly trustworthy.

The value for the amount of corpuscular radiation liberated in the gas was in each case calculated for the amount of gas or vapour actually present. These values must then be reduced to what they would be at atmospheric pressure, for purposes of comparison. As, however, it has been abundantly shown that ionisation varies strictly in proportion to the pressure,† this correction is simple to apply. The values of A_1/A_0 corrected for absorption and for pressure are given in column VII, Table I.

Table I.

Substance.	Pressure at which used, in om. of Hg.	Ionisation in cyl. chamber corrected for ends. (Air == 1.) II.	Corpuscular factor observed.	True corpus-cular factor. k.	Corpuscles liberated from gas in chamber. (Air = 1.)	A_1/A_0 .	A ₁ /A ₀ calculated for 76 cm, of Hg. VII.
Nitrous oxide	76 .0	1 ·32	1 .02	1 .02	1 .29	1 .32	1 .32
Carbon di- oxide	76 ∙0	1 ·48	1 .02	1 .02	1 '40	1 44	1 '44
Ammonia	76 0	0.42	1 .22	1 .22	0.34(5)	0.33(3)	0.83(3)
Carbon disul- phide (and hydrogen)	12 8	4.00	1 '25(5)	1 ·26	8 ·17	8.70	21 9(5)
Chloroform (and hydro- gen)	6.2	3 ·22	1 .01	1 '01(5)	3·18	3 ·72	43 ·5
Hydrochloric	76 ·0	8.6	1 ·15(5)	1 ·16(5)	7 .41	15 .2	15 .2
Carbon tetra- chloride (and hydro- gen)	3 · 29 5	2 · 44	^1 1 ·07	1 '07(5)	2 ·27	2 54	58 ·6

^{* &#}x27;Phys. Sec. Proc.,' 1914.

[†] Crowther, 'Camb. Phil. Soc. Proc.,' February, 1909; and Owen, 'Roy. Soc. Proc.,' May, 1912.

The final values for A_1/A_0 having been calculated for each of the gases at atmospheric pressure, equations were found expressing the corpuscular radiation in the gas (air = 1) as the sum of the atomic corpuscular radiations of the constituents of the gas. Thus, if C, N, O, S and Cl represent the amounts of corpuscular radiation from atoms of carbon nitrogen, oxygen, etc. respectively, air being taken as emitting unit quantity, we have:—

Nitrous oxide	2N + 0	=	1.32
Carbon dioxide	C + 2O	=	1.44
Ammonia	N + 3H	=	0.33(3)
Carbon disulphide	C + 2S	=	21.95
Chloroform	C + H + 3Cl	=	43·5
Hydrochloric acid	H + Cl	=	15.2
Carbon tetrachloride	C + 4Cl	=	58· 6

The values of C and O obtained in the previous paper were C = 0.2 and O = 0.62 respectively. These agree exactly with the value for carbon dioxide given above. Accepting these values for C and O, and considering H = 0 we obtain the following values:—

From (1)
$$2N = 1.32 - 0.62$$
, whence $N = 0.35$ similarly (3) gives $N = 0.33$ (3) $N = 0.33$ (4) $2S = 21.75$ $S = 10.9$ (5) $3Cl = 43.3$ $Cl = 14.4$ (6) $Cl = 15.2$ $Cl = 15.2$ (7) $4Cl = 58.4$ $Cl = 14.6$

The extreme difference for both the nitrogen and chlorine values is less than 7 per cent. In the case of nitrogen the possible error was estimated a from 7 to 10 per cent. from the true value, on account of the relatively small value of the ionisations observed and of the difficulties peculiar to the handling of ammonia. For chlorine a similar range of error was estimated, on account of the large correction that has to be applied for absorption. The errors are in no case 4 per cent. from the mean, so that any difference in the values obtained are well within the errors of experiment.

The value obtained for sulphur can be compared with that deduced from the observations by Barkla and Philpot, and shows a remarkably close agreement. For SH_2 the ionisation (air = 1) for copper radiation is 14.7, the corpuscular factor is 1.33, giving S+2H=11.0, i.e. S=11.0. For SO_2 they obtained an ionisation 11.5 and a corpuscular factor 0.96, so that S+2O=12.0, i.e. S=10.8. This close agreement with the value

obtained in the present series of experiments for sulphur in carbon disulphide, demonstrates that the corpuscular radiation from the atom is independent of the chemical combination in the case of sulphur also.

An interesting relation between the corpuscular radiation emitted by the atom in a given beam of X-rays and the atomic weight of the substance may be mentioned. It will be observed that the quantity of corpuscular radiation emitted increases very rapidly with the atomic weight. The values of these radiations from the various elements obey very closely a fourth-power law. This will be seen from the following Table, in which (Column 4) the quotient of the fourth power of the atomic weight, divided by the corpuscular radiation from the atom (air = 1) is given:—

(Atomic weight)⁴ \times 10⁻⁴. Atomic corpuscular (Atomic weight)4 Substance radiation (A.C.R.). × 10⁻⁴. and atomic weight. A.C.R. Air 🖮 T. Carbon (12); 0.2 2:07 10.3 Nitrogen (14) 0.343 .84 11 3 0.626 '55 10 .4 Oxygen (16) Sulphur (32) 10 9 104 8 9 .6 10.8 Chlorine (35.5) ... 14 7 158 8

Table II.

The variation in the last column is not greater than 8 per cent. from the mean, and although this is fairly considerable the agreement is of such a nature as to suggest that a fourth-power law is probably correct. Further investigations are being prosecuted with a view to obtaining additional evidence on this point.

The statement made on p. 340 that λ is proportional to A, for a given substance subjected to a beam of X-rays of definite wave-length, is deduced from the results of Barkla and Simons' and Barkla and Philpot's work.

Total or equal absorptions of X-radiations in two gases produce ionisations in the same ratio as the ionisations due to the absorptions of equal amounts of electronic radiation in the same two gases. The energy of the X-radiation absorbed, therefore, is spent in the liberation of electronic radiation, in exact proportion to the amount of X-radiation absorbed, if indeed the whole of the energy lost is not converted into this form of radiation. If, therefore, we obtain a quantity of electronic radiation A per centimetre of length of path in a gas, when a beam of X-radiation is passed through it, we may conclude that the quantity of the X-radiation absorbed per centimetre is proportional to A, i.e. that the linear absorption coefficient λ in the gas is proportional to A.

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This being so, the coefficient of absorption for a given type of radiation in a gas will be atomic, even as A is atomic, a result obtained by Benoist as early as 1901. Also, the absorption due to any atom will vary directly as the fourth power of its atomic weight. The importance of this law is considerable, as it will enable the coefficient of absorption for a given type of radiation in any gas or vapour to be calculated, provided the coefficient of absorption of that radiation in air or some other gas has been obtained.

This fourth-power law is not limited to gases and vapours, Prof. Bragg and S. E. Pierce* having recently shown that it is true for solids. In their work, the coefficient of absorption is compared with the fourth power of the atomic number of the absorbing element, an approximately constant relation being found between these quantities for a number of elemental solids.

The results obtained in the present paper are not sufficiently accurate to differentiate between the two suggested laws, and the fourth power of the atomic weight has been used in the calculations, to indicate the sort of way in which the atomic corpuscular radiation and the atomic absorption coefficients vary, and not as claiming an absolute law.

Whichever of these laws is true, it holds for both vapours and solids; it is therefore doubtless true for liquids also, and hence it should be possible to calculate the absorption coefficients in any material whether solid, liquid or gaseous.

Preliminary calculations on this assumption suggest that it is of quite general application, provided the homogeneous radiation of the absorbing element is not excited: the whole question is under further investigation.

Conclusions and Abstract.

In a former paper it was shown that, for carbon and oxygen, the number of corpuscles liberated from an atom by a beam of X-rays was the same whether the atom is in combination or not. This conclusion has been extended to the cases of nitrogen, sulphur, and chlorine, a close agreement being obtained for each of these in two or three different combinations respectively; the values previously obtained for carbon and oxygen have also been corroborated.

In addition, it is shown that the atomic corpuscular radiation, i.e. the corpuscular radiation from an atom, is approximately proportional to the fourth power of the weight of the atom, the deviations in the observed values from this fourth-power law being of such a character as to suggest that they are merely due to experimental errors.

From the observations of Barkla and Simons and Barkla and Philpot, it is shown that the coefficient of absorption of a beam of X-radiation in a gas is proportional to the quantity of electronic radiation liberated from the gas, and hence the X-radiation absorbed by an atom of a given element will also be proportional to the fourth power of the weight of the absorbing atom. Recent experiments of Bragg and Pierce show that a similar law holds good for elements in the solid state, and is therefore probably of universal application: it should therefore be possible to calculate the absorption coefficient of any material, provided its homogeneous radiation is not excited.

These points are under further investigation.

I should like to express my indebtedness to Prof. O. W. Richardson for the interest he has taken in these investigations, and for the facilities he has provided for their furtherance.

Deep Water Waves, Progressive or Stationary, to the Third Order of Approximation.

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As is well known, the form of periodic waves progressing over deep water without change of type was determined by Stokes* to a high degree of approximation. The wave-length (λ) in the direction of x being 2π and the velocity of propagation unity, the form of the surface is given by

$$y = a\cos(x-t) - \frac{1}{2}a^2\cos 2(x-t) + \frac{3}{2}a^3\cos 3(x-t), \tag{1}$$

and the corresponding gravity necessary to maintain the motion by

$$q = 1 - a^2. \tag{2}$$

The generalisation to other wave-lengths and velocities follows by dimensions."

These and further results for progressive waves of permanent type are most easily arrived at by use of the stream-function on the supposition that the waves are reduced to rest by an opposite motion of the water as a whole, when the problem becomes one of steady motion.† My object at present is

^{* &#}x27;Camb. Phil. Trans.,' vol. 8, p. 441 (1847); 'Math. and Phys. Papers,' vol. 1, p. 197.

^{† &#}x27;Phil. Mag.,' vol. 1, p. 257 (1876); 'Scientific Papers,' vol. 1, p. 262. Also 'Phil. Mag.,' vol. 21, p. 183 (1911).

to extend the scope of the investigation by abandoning the initial restriction to progressive waves of permanent type. The more general equations may then be applied to progressive waves as a particular case, or to stationary waves in which the principal motion is proportional to a simple circular function of the time, and further to ascertain what occurs when the conditions necessary for the particular cases are not satisfied. Under these circumstances the use of the stream-function loses much of its advantage, and the method followed is akin to that originally adopted by Stokes.

The velocity-potential ϕ , being periodic in x, may be expressed by the series

$$\phi = \alpha e^{-y} \sin x - \alpha' e^{-y} \cos x + \beta e^{-2y} \sin 2x - \beta' e^{-2y} \cos 2x + \gamma e^{-3y} \sin 3x - \gamma' e^{-3y} \cos 3x + \dots,$$
 (3)

where α , α' , β , etc., are functions of the time only, and y is measured downwards from mean level. In accordance with (3) the component velocities are given by

$$u = d\phi/dx = e^{-y} (\alpha \cos x + \alpha' \sin x) + 2e^{-2y} (\beta \cos 2x + \beta' \sin 2x) + \dots$$
$$-v = d\phi/dy = e^{-y} (\alpha \sin x - \alpha' \cos x) + 2e^{-2y} (\beta \sin 2x - \beta' \cos 2x) + \dots$$

The density being taken as unity, the pressure equation is

$$p = -d\phi/dt + F + gy - \frac{1}{2}(u^2 + v^2), \tag{4}$$

in which F is a function of the time.

In applying (4) we will regard α , α' , as small quantities of the first order, while β , β' , γ , γ' , are small quantities of the second order at most; and for the present we retain only quantities of the second order. β , etc., will then not appear in the expression for $n^2 + r^2$. In fact

$$u^2 + v^2 = e^{-2y} (\alpha^2 + \alpha'^2),$$

and

$$p = -\frac{d\alpha}{dt}e^{-y}\sin x + \frac{d\alpha'}{dt}e^{-y}\cos x - \frac{d\beta}{dt}e^{-2y}\sin 2x + \dots + gy - \frac{1}{2}e^{-2y}(\alpha^2 + \alpha'^2) + F.$$
 (5)

The surface conditions are (i) that p be there zero, and (ii) that

$$\frac{\mathrm{D}p}{\mathrm{D}t} = \frac{dp}{dt} + u\frac{dp}{dx} + v\frac{dp}{dy} = 0. \tag{6}$$

The first is already virtually expressed in (5). For the second

$$\begin{aligned} \frac{dp}{dt} &= -\frac{d^2\alpha}{dt^2} e^{-y} \sin x + \frac{d^3\alpha'}{dt^2} e^{-y} \cos x - \dots - e^{-2y} \left(\alpha \frac{d\alpha}{dt} + \alpha' \frac{d\alpha'}{dt} \right) + F', \\ \frac{dp}{dx} &= -\frac{d\alpha}{dt} e^{-y} \cos x - \frac{d\alpha'}{dt} e^{-y} \sin x - \dots, \\ \frac{dp}{dy} &= \frac{d\alpha}{dt} e^{-y} \sin x - \frac{d\alpha'}{dt} e^{-y} \cos x + \dots + g + e^{-2y} \left(\alpha^2 + \alpha'^2 \right). \end{aligned}$$

In forming equation (6) to the second order of small quantities we need to include only the principal term of u, but v must be taken correct to the second order. As the equation of the free surface we assume

 $y = a\cos x + a'\sin x + b\cos 2x + b'\sin 2x + c\cos 3x + c'\sin 3x + \dots$ (7) in which b, b', c, c', are small compared with a, a'. Thus (6) gives

$$(1 - a\cos x - a'\sin x) \left(-\frac{d^2\alpha}{dt^2}\sin x + \frac{d^2\alpha'}{dt^2}\cos x \right) - \frac{d^2\beta}{dt^2}\sin 2x$$

$$+ \frac{d^2\beta'}{dt^2}\cos 2x - \frac{d^2\gamma}{dt^2}\sin 3x + \frac{d^2\gamma}{dt^2}\cos 3x - \alpha\frac{d\alpha}{dt} - \alpha'\frac{d\alpha'}{dt} + F'$$

$$- (\alpha\cos x + \alpha'\sin x) \left(\frac{d\alpha}{dt}\cos x + \frac{d\alpha'}{dt}\sin x \right) - \left\{ (1 - a\cos x - \alpha'\sin x) \right\}$$

$$\times (\alpha\sin x - \alpha'\cos x) + 2\beta\sin 2x - 2\beta'\cos 2x + 3\gamma\sin 3x - 3\gamma'\cos 3x$$

$$\times \left\{ g + \frac{d\alpha}{dt}\sin x - \frac{d\alpha'}{dt}\cos x \right\} = 0.$$
(8)

This equation is to hold good to the second order for all values of x, and therefore for each Fourier component separately. The terms in $\sin x$ and $\cos x$ give

$$\frac{d^2\alpha}{dt^2} + g\alpha = 0, \qquad \frac{d^2\alpha'}{dt^2} + g\alpha' = 0. \tag{9}$$

The term in $\sin 2x$ gives

$$\frac{d^2\beta}{dt^2} + 2g\beta = \frac{a}{2} \left(\frac{d^2\alpha}{dt^2} + g\alpha \right) - \frac{a'}{2} \left(\frac{d^2\alpha'}{dt^2} + g\alpha' \right) = 0, \tag{10}$$

and, similarly, that in $\cos 2x$ gives

$$\frac{d^2\beta'}{dt^2} + 2g\beta' = 0. \tag{11}$$

In like manner

$$\frac{d^2\gamma}{dt^2} + 3g\gamma = 0, \qquad \frac{d^2\gamma'}{dt^2} + 3g\gamma' = 0, \tag{12}$$

and so on. These are the results of the surface condition Dp/Dt = 0. From the other surface condition (p = 0) we find in the same way

$$-\frac{d\alpha}{dt} + g\alpha' = 0, \qquad \frac{d\alpha'}{dt} + g\alpha = 0. \tag{13}$$

$$gb' = \frac{d\beta}{dt} + \frac{a'}{2}\frac{d\alpha'}{dt} - \frac{a}{2}\frac{d\alpha}{dt} = \frac{d\beta}{dt} - gaa'.$$
 (14)

$$gb = -\frac{d\beta}{dt} + \frac{a'}{2}\frac{d\alpha}{dt} + \frac{a}{2}\frac{d\alpha'}{dt} = -\frac{d\beta}{dt} + \frac{1}{2}g(\alpha'^2 - \alpha^2). \tag{15}$$

$$-\frac{d\gamma}{dt} + gc' = 0, \qquad \frac{d\gamma'}{dt} + gc = 0. \tag{16}$$

From equations (9) to (16) we see that a, a', satisfy the same equations (9) as do α , α' , and also that c, c', satisfy the same equations (12) as do γ , γ' ; but that b, b', are not quite so simply related to β , β' .

Let us now suppose that the principal terms represent a progressive wave. In accordance with (9) we may take

$$a = A \cos t', \qquad a' = A \sin t', \qquad (17)$$

where $t' = \sqrt{g \cdot t}$. Then if β , β' , γ , γ' , do not appear, c, c', are zero, and $b = \frac{1}{2} A^2 (\sin^2 t' - \cos^2 t')$, $b' = -A^2 \cos t' \sin t'$; so that

$$y = A\cos(x-t') - \frac{1}{2}A^2\cos 2(x-t'), \tag{18}$$

representing a permanent wave-form propagated with velocity \sqrt{g} . So far as it goes, this agrees with (1). But now in addition to these terms we may have others, for which b, b' need only to satisfy

$$(d^2/dt'^2 + 2)(b, b') = 0, (19)$$

and c, c', need only to satisfy

$$(d^2/dt'^2 + 3)(c, c') = 0. (20)$$

The corresponding terms in y represent merely such waves, propagated in either direction, and of wave-lengths equal to an aliquot part of the principal wave-length, as might exist alone of infinitesimal height, when there is no primary wave at all. When these are included, the aggregate, even though it be all propagated in the same direction, loses its character of possessing a permanent wave shape, and further it has no tendency to acquire such a character as time advances.

If the principal wave is stationary we may take

$$\alpha = A \cos t', \qquad \alpha' = 0. \tag{21}$$

If β , β' , γ , γ' , vanish,

$$b = -\frac{1}{2}a^2$$
, $b' = 0$, $c = 0$, $c' = 0$,

and

$$y = A \cos x \cdot \cos t' - \frac{1}{2} A^2 \cos 2x \cdot \cos^2 t'.$$
 (22)

According to (22) the surface comes to its zero position everywhere when $\cos t' = 0$, and the displacement is a maximum when $\cos t' = \pm 1$. Then

$$y = \pm A \cos x - \frac{1}{2} A^2 \cos 2x, \qquad (23)$$

so that at this moment the wave-form is the same as for the progressive wave (18). Since y is measured downwards, the maximum elevation above the mean level exceeds numerically the maximum depression below it.

In the more general case (still with β , etc., evanescent) we may write

$$\alpha = A \cos t' + B \sin t'$$
, $\alpha' = A' \cos t' + B' \sin t'$,

with
$$b' = -aa'$$
, $b = \frac{1}{2}(a'^2 - a^2)$, $c' = 0$, $c = 0$.

When β , β' , γ , γ' , are finite, waves such as might exist alone, of lengths equal to aliquot parts of the principal wave-length and of corresponding frequencies, are superposed. In these waves the amplitude and phase are arbitrary.

When we retain the third order of small quantities, the equations naturally become more complicated. We now assume that in (3) β , β' , are small quantities of the second order, and γ , γ' , small quantities of the third order. For p, as an extension of (5), we get

$$p = e^{-y} \left(-\frac{d\alpha}{dt} \sin x + \frac{d\alpha'}{dt} \cos x \right) + e^{-2y} \left(-\frac{d\beta}{dt} \sin 2x + \frac{d\beta'}{dt} \cos 2x \right)$$
$$+ e^{-3y} \left(-\frac{d\gamma}{dt} \sin 3x + \frac{d\gamma'}{dt} \cos 3x \right) + gy + \mathbf{F} - \frac{1}{2} e^{-2y} \left(\alpha^2 + \alpha'^2 \right)$$
$$-2e^{-3y} \left\{ (\alpha\beta + \alpha'\beta') \cos x + (\alpha\beta' - \alpha'\beta) \sin x \right\}. \tag{24}$$

This is to be made to vanish at the surface. Also we find, on reduction,

$$-\frac{\mathrm{D}p}{\mathrm{D}t} = (1 - y + \frac{1}{2}y^{2}) \left\{ \left(\frac{d^{2}\alpha}{dt^{2}} + g\alpha \right) \sin x - \left(\frac{d^{2}\alpha'}{dt^{2}} + g\alpha' \right) \cos x \right\}$$

$$+ (1 - 2y) \left\{ \left(\frac{d^{2}\beta}{dt^{2}} + 2g\beta \right) \sin 2x - \left(\frac{d^{2}\beta'}{dt^{2}} + 2g\beta' \right) \cos 2x \right\}$$

$$+ \left(\frac{d^{3}\gamma}{dt^{2}} + 3g\gamma \right) \sin 3x - \left(\frac{d^{2}\gamma'}{dt^{2}} + 3g\gamma' \right) \cos 3x - \mathrm{F}'$$

$$+ 2\left(1 - 2y \right) \left(\alpha \frac{d\alpha}{dt} + \alpha' \frac{d\alpha'}{dt} \right) + 4 \sin x \frac{d}{dt} \left(\alpha\beta' - \alpha'\beta \right)$$

$$+ 4 \cos x \frac{d}{dt} \left(\alpha\beta' + \alpha'\beta \right) + \left(\alpha^{2} + \alpha'^{2} \right) \left(\alpha \sin x - \alpha' \cos x \right); \tag{25}$$

and at the surface Dp/Dt = 0 for all values of x. In (25) y is of the form (7), where b, b', are of the second order, c, c', of the third order.

Considering the coefficients of $\sin x$, $\cos x$, in (25) when reduced to Fourier's form, we see that $d^2\alpha/dt^2+g\alpha$, $d^2\alpha'/dt^2+g\alpha'$, are both of the third order of small quantities, so that in the first line the factor $(1-y+\frac{1}{2}y^2)$ may be replaced by unity. Again, from the coefficients of $\sin 2x$, $\cos 2x$, we see that to the third order inclusive

$$\frac{d^2\beta}{dt^2} + 2g\beta = 0, \qquad \frac{d^2\beta'}{dt^2} + 2g\beta' = 0, \tag{26}$$

and from the coefficients of sin 3x, cos 3x, that to the third order inclusive

$$\frac{d^2\gamma}{dt^2} + 3g\gamma = 0, \qquad \frac{d^2\gamma'}{dt^2} + 3g\gamma' = 0. \tag{27}$$

And now returning to the coefficients of $\sin x$, $\cos x$, we get

$$\frac{d^2\alpha}{dt^2} + g\alpha - 2\alpha' \frac{d}{dt} (\alpha^2 + \alpha'^2) + 4\frac{d}{dt} (\alpha\beta' - \alpha'\beta) + \alpha(\alpha^2 + \alpha'^2) = 0, \quad (28)$$

$$\frac{d^2\alpha'}{dt^2} + g\alpha' + 2\alpha \frac{d}{dt}(\alpha^2 + \alpha'^2) - 4\frac{d}{dt}(\alpha\beta' + \alpha'\beta) + \alpha'(\alpha^2 + \alpha'^2) = 0.$$
 (29)

Passing next to the condition p = 0, we see from (24), by considering the coefficients of $\sin x$, $\cos x$, that

$$-\frac{d\alpha}{dt} + g\alpha' + \text{terms of 3rd order} = 0,$$

$$\frac{d\alpha'}{dt} + g\alpha + \text{terms of 3rd order} = 0.$$

 $\frac{dt}{dt} + ga + \text{terms of 3rd order} = 0.$

The coefficients of $\sin 2x$, $\cos 2x$, require, as in (14), (15), that

$$b' = \frac{1}{g} \frac{d\beta}{dt} - aa', \qquad b = -\frac{1}{g} \frac{d\beta'}{dt} + \frac{a'^2 - a^2}{2}.$$
 (30)

Again, the coefficients of $\sin 3x$, $\cos 3x$, give

$$c' = \frac{1}{g} \frac{d\gamma}{dt} - \frac{3}{2} (a'b + ab') + \frac{3}{8} a' (a'^2 - 3a^2)$$

$$= \frac{1}{g} \left\{ \frac{d\gamma}{dt} - \frac{3a}{2} \frac{d\beta}{dt} + \frac{3a'}{2} \frac{d\beta'}{dt} \right\} - \frac{3a'}{8} (a'^2 - 3a^2), \tag{31}$$

$$c = -\frac{1}{g} \frac{d\gamma'}{dt} + \frac{3}{2} (a'b' - ab) + \frac{3a}{8} (3a'^2 - a^2)$$

$$= \frac{1}{a} \left\{ -\frac{d\gamma'}{dt} + \frac{3a'}{2} \frac{d\beta}{dt} + \frac{3a}{2} \frac{d\beta'}{dt} \right\} - \frac{3a}{8} (3a'^2 - a^2). \tag{32}$$

When β , β' , γ , γ' , vanish, these results are much simplified. We have

$$b' = -aa', b = \frac{1}{2}(a'^2 - a^2), (33)$$

$$c' = -\frac{3a'}{8}(a'^2 - 3a^2), \qquad e = -\frac{3a}{8}(3a'^2 - a^2).$$
 (34)

If the principal terms represent a purely progressive wave, we may take, as in (17),

$$a = A \cos nt, \qquad a' = A \sin nt,$$
 (35)

where n is for the moment undetermined. Accordingly

$$b' = -\frac{1}{2}A^2 \sin 2nt,$$
 $b = -\frac{1}{2}A^2 \cos 2nt,$ $c' = \frac{3}{4}A^3 \sin 3nt,$ $c = \frac{3}{4}A^3 \cos 3nt;$

so that

$$y = A\cos(x - nt) - \frac{1}{2}A^{2}\cos 2(x - nt) + \frac{3}{2}A^{3}\cos 3(x - nt), \tag{36}$$

representing a progressive wave of permanent type, as found by Stokes.

To determine n we utilise (28), (29), in the small terms of which we may take

$$\alpha = g \int a'dt = -\frac{g\mathbf{A}}{n}\cos nt, \qquad \alpha' = -g \int a\,dt = -\frac{g\mathbf{A}}{n}\sin nt,$$

so that

$$\alpha^2 + \alpha'^2 = g^2 A^2/n^2.$$

Thus

$$\frac{d^2(\alpha, \alpha')}{dt^2} + \left(g + \frac{g^2 \mathbf{A}^2}{n^2}\right)(\alpha, \alpha') = 0,$$

and

$$n^2 = g + g^2 A^2 / n^2 = g(1 + A^2),$$
 (37)

or, if we restore homogeneity by introduction of $k = 2\pi/\lambda$,

$$u^2 = g/k \cdot (1 + k^2 A^3).$$
 (38)

Let us next suppose that the principal terms represent a stationary, instead of a progressive, wave and take

$$a = A \cos nt, \qquad a' = 0. \tag{39}$$

Then by (33), (34),

$$b' = 0$$
, $b = -\frac{1}{3} A^2 \cos^2 nt$, $c' = 0$, $c = \frac{3}{3} A^3 \cos^3 nt$;

and

$$y = A\cos nt\cos x - \frac{1}{2}A^{2}\cos^{2}nt\cos 2x + \frac{3}{8}A^{3}\cos^{3}nt\cos 3x.$$
 (40)

When $\cos nt = 0$, y = 0 throughout; when $\cos nt = 1$,

$$y = A \cos x - \frac{1}{2} A^2 \cos 2x + \frac{3}{8} A^3 \cos 3x$$

so that at this moment of maximum displacement the form is the same as for the progressive wave (36).

We have still to determine n so as to satisfy (28), (29), with evanescent β , β' . The first is satisfied by $\alpha = 0$, since $\alpha' = 0$. The second becomes

$$\frac{d^2\alpha'}{dt^2} + g\alpha' + 4\alpha\alpha' \frac{d\alpha'}{dt} + \alpha'^3 = 0.$$

In the small terms we may take $\alpha' = -g \int a \, dt = -\frac{gA}{n} \sin nt$, so that

$$\frac{d^2\alpha'}{dt^2} + g\alpha' + \frac{g^2\mathbf{A}^3}{4n}(\sin nt + 5\sin 3nt) = 0.$$

To satisfy this we assume

$$\alpha' = H \sin nt + K \sin 3nt$$

Then

$$H(g-n^2) + \frac{g^2A^3}{4n} = 0$$
, $K(g-9n^2) + \frac{5g^2A^3}{4n} = 0$,

from the first of which

$$n^{3} = g + \frac{g^{2}A^{3}}{4nH} = g - \frac{gA^{2}}{4}, \tag{41}$$

or, if we restore homogeneity by introduction of k,

$$n^2 = g/k \cdot (1 - \frac{1}{4}k^2 A^2). \tag{42}$$

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With this value of n the stationary vibration

 $y = A \cos nt \cos kx - \frac{1}{2}kA^2 \cos^2 nt \cos 2kx + \frac{3}{8}k^3A^3 \cos^3 nt \cos 3kx$, (43) satisfies all the conditions. It may be remarked that according to (42) the frequency of vibration is diminished by increase of amplitude.

The special cases above considered of purely progressive or purely stationary waves possess an exceptional simplicity. In general, with omission of β , β' , equations (28), (29), become

$$\frac{d^2\alpha}{dt^2} + g\alpha - \frac{2}{g} \frac{d\alpha}{dt} \frac{d(\alpha^2 + \alpha'^2)}{dt} + \alpha(\alpha^2 + \alpha'^2) = 0, \tag{44}$$

and a like equation in which α and α' are interchanged. In the terms of the third order, we take

$$\alpha = P \cos nt + Q \sin nt, \qquad \alpha' = P' \cos nt + Q' \sin nt,$$
 (45)

so that

$$\begin{split} \alpha^2 + \alpha'^2 &= \frac{1}{2} \left(\mathbf{P}^2 + \mathbf{Q}^2 + \mathbf{P}'^2 + \mathbf{Q}'^2 \right) + \frac{1}{2} \left(\mathbf{P}^2 + \mathbf{P}'^2 - \mathbf{Q}^2 - \mathbf{Q}'^2 \right) \cos 2nt \\ &+ \left(\mathbf{P} \mathbf{Q} + \mathbf{P}' \mathbf{Q}' \right) \sin 2nt. \end{split}$$

The third order terms in (44) are

$$\begin{split} &\frac{1}{2} \left(\mathbf{P^2} + \mathbf{P'^2} + \mathbf{Q^2} + \mathbf{Q'^2} \right) \left(\mathbf{P} \cos nt + \mathbf{Q} \sin nt \right) \\ &+ 2 \cos nt \cos 2nt \, \left\{ \frac{1}{4} \, \mathbf{P} \left(\mathbf{P^2} + \mathbf{P'^2} - \mathbf{Q^2} - \mathbf{Q'^2} \right) - \frac{2n^2\mathbf{Q}}{g} \left(\mathbf{PQ} + \mathbf{P'Q'} \right) \right\} \\ &+ 2 \sin nt \sin 2nt \, \left\{ \frac{1}{4} \, \mathbf{Q} \left(\mathbf{PQ} + \mathbf{P'Q'} \right) - \frac{n^2\mathbf{P}}{g} \left(\mathbf{P^2} + \mathbf{P'^2} - \mathbf{Q^2} - \mathbf{Q'^2} \right) \right\} \\ &+ 2 \sin nt \cos 2nt \, \left\{ \frac{1}{4} \, \mathbf{Q} \left(\mathbf{P^2} + \mathbf{P'^2} - \mathbf{Q^2} - \mathbf{Q'^2} \right) + \frac{2n^2\mathbf{P}}{g} \left(\mathbf{PQ} + \mathbf{P'Q'} \right) \right\} \\ &+ 2 \cos nt \sin 2nt \, \left\{ \frac{1}{2} \, \mathbf{P} \left(\mathbf{PQ} + \mathbf{P'Q'} \right) + \frac{n^2\mathbf{Q}}{g} \left(\mathbf{P^2} + \mathbf{P'^2} - \mathbf{Q^2} - \mathbf{Q'^2} \right) \right\} \,, \end{split}$$

of which the part in sin nt has the coefficient

$$Q \{ \frac{1}{4} (P^2 + P'^2) + \frac{3}{4} (Q^2 + Q'^2) \} + \frac{1}{2} P (PQ + P'Q') + n^2/g \cdot \{ Q (P^2 + P'^2 - Q^2 - Q'^2) - 2 P (PQ + P'Q') \},$$

or, since $n^2 = g$ approximately,

$$Q\left\{\frac{5}{4}(P^{2}+P'^{2})-\frac{1}{4}(Q^{2}+Q'^{2})\right\}-\frac{3}{2}P(PQ+P'Q'). \tag{46}$$

In like manner the coefficient of cos nt is

$$P\left\{\frac{5}{4}(Q^{2}+Q'^{2})-\frac{1}{4}(P^{2}+P'^{2})\right\}-\frac{3}{2}Q(PQ+P'Q'),\tag{47}$$

differing merely by the interchange of P and Q.

But when these values are employed in (44), it is not, in general, possible, with constant values of P, Q, P', Q', to annul the terms in $\sin nt$, $\cos nt$. We obtain from the first

$$n^{2} = g + \frac{5}{4} (P^{2} + P'^{2}) - \frac{1}{4} (Q^{2} + Q'^{2}) - \frac{3P}{2Q} (PQ + P'Q'), \tag{48}$$

and from the second

$$n^{9} = g + \frac{5}{4} (Q^{2} + Q'^{2}) - \frac{1}{4} (P^{9} + P'^{2}) - \frac{3Q}{2P} (PQ + P'Q'); \qquad (49)$$

and these are inconsistent, unless

$$(PP' + QQ')(PQ' - P'Q) = 0. (50)$$

The latter condition is unaltered by interchange of dashed and undashed letters, and thus it serves equally for the equation in α' .

The two alternatives indicated in (50) correspond to the particular cases already considered. In the first (PP' + QQ' = 0) we have a purely progressive wave and in the second a purely stationary one.

When the condition (50) does not hold good, it is impossible to satisfy our equations as before with constant values of n, P, Q, P', Q'; and it is perhaps hardly worth while to pursue the more complicated questions which then arise. It may suffice to remark that an approximately stationary wave can never pass into an approximately progressive wave, nor *vice versa*. The progressive wave has momentum, while the stationary wave has none, and momentum is necessarily conserved.

When β , β' , γ , γ' , are not zero, additional terms enter. Equations (26), (30), show that the additions to b, b', vary as the sine and cosine of $\sqrt{(2g)}$. t, and represent waves which might exist in the complete absence of the principal wave.

The additions to c, c', are more complicated. As regards the parts depending in (31), (32), on $d\gamma/dt$, $d\gamma'/dt$, they are proportional to the sine and cosine of $\sqrt{(3g)}$. t, and represent waves which might exist alone. But besides these there are other parts, analogous to the combination-tones of Acoustics, resulting from the interaction of the β -waves with the principal wave. These vary as the sine and cosine of \sqrt{g} . $\{\sqrt{2\pm 1}\}$ t, thus possessing frequencies differing from the former frequencies. Similar terms will enter into the expression for n^2 as determined from (28), (29).

In the particular case of β , β' , vanishing, even though γ , γ' (assumed still to be of the third order), remain, we recover most of the former simplicity, the only difference being the occurrence in c, c', of terms in $\sqrt{(3g)} \cdot t$, such as might exist alone.

Discontinuous Fluid Motion past a Bent Plane, with Special Reference to Aeroplane Problems.

By G. H. BRYAN, Sc.D., F.R.S., and ROBERT JONES, M.A.

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The following investigation is based on the Kirchhoff-Helmholtz theory of discontinuous stream-line motion of a fluid moving through an orifice or past a barrier. The problem is two-dimensional and the fluid is assumed to be frictionless and incompressible.

The question has been discussed fully by Sir G. Greenhill, F.R.S., in his report to the Advisory Committee for Aeronautics, and in his book on the Dynamics of Mechanical Flight. He considers at length the fluid motion past a barrier, but in what follows a bent barrier will be considered.

Greenhill refers to a problem similar to this, where the stream is supposed to divide at the bend. The present case can be reduced to that one, by making two parametric angles equal (P = B).

Integrals are obtained giving the lengths of and thrusts on the planes, and by means of approximate methods these will be evaluated. It will also be shown how these integrals can be evaluated exactly, but the expressions to which they have been reduced are so long that they cannot be of great value in investigating special cases.

The results arrived at will be used in finding the lift and drift on the surface, and the relative advantages of planes bent at different angles and along different lines (parallel to the edges) will be considered.

Supposing the surface to be the main plane of an aeroplane, and the fluid to be air, the numerical results cannot be expected to be strictly quantitatively correct, inasmuch as the motion is supposed two-dimensional and the fluid here considered is assumed to be frictionless and incompressible, which is by no means true for actual fluids. Consequently, instead of a region of dead water, separated by a surface of discontinuity from the moving part, eddies are set up in the wake of a surface moving through air.

Qualitative conclusions can, however, be drawn, and the effect of camber compared for various planes, and in this respect our results appear to agree with experimental results.

§ 1. List of the Functions employed.

Although the theory of discontinuous motion is well known and explained, not always very lucidly, in text-books, it will be convenient to briefly summarise the functions and transformations employed, as follows:—

z = x + iy; x and y are the co-ordinates of a point in the z diagram, being a representation of the cross section of the planes and the fluid.

 $w = \phi + i\psi$; ϕ velocity potential, ψ stream function. In the w diagram lines parallel to the real axis represent the stream-lines.

 $\zeta = Q(dz/dw)$, where Q is the velocity at infinity,

mod $\zeta = Q/q$, where q is the resultant velocity at any point,

 $\arg \zeta = \theta$, the directional angle of this velocity,

$$\Omega = \log \zeta = \log (Q/q) + i\theta.$$

In the Ω diagram fixed straight boundaries are represented by the lines $\theta = \text{constant}$ parallel to the real axis, and free boundaries of surfaces of discontinuity by straight lines parallel to the imaginary axis (since by the pressure equation q is constant) usually by the imaginary axis itself $\log (Q/q) = 0$ corresponding to q = Q.

In the case of a stream of infinite breadth impinging on a single barrier, and dividing, at a point P in the barrier, into parts flowing past the two sides, the dividing stream line in the w diagram invariably takes the form shown in fig. 3 (§ 2), and it is necessary to apply the transformation $t = \sqrt{w}$ in order to reduce the diagram to the form of fig. 4 (§ 2), the angle between PD and PE thus being changed from 360° to 180° .

This transformation is, of course, a case of the Schwarz-Christoffel transformation

$$d\Omega/dt = \text{const.}(t-a)^{a/\pi-1}(t-b)^{6/\pi-1}(t-c)^{\gamma/\pi-1}...,$$
*

by means of which points on the sides AB, BC, ..., A of a closed rectilinear polygon in the Ω diagram are represented by points on the real axis in the t diagram; a, b, c, etc., corresponding to the corners A, B, C, etc., of the polygon at which the internal angles are α , β , γ , etc. Points within the polygon are represented by points in the positive half plane in t.

As t increases through the value a say the corresponding factor of the modulus changes from $(a-t)^{a/\pi-1}$ to $(t-a)^{a/\pi-1}$, i.e. a factor $(-1)^{a/\pi-1}$ is added to $d\Omega/dt$, so that the argument in the Ω diagram changes by $\pi-\alpha$.

The formula can of course be written

$$d\Omega/dt = \text{const.}(t-a)^{a'/\pi}(t-b)^{\beta'/\pi}...,$$

 α' , β' , etc., being the external angles corresponding to α , β , etc.

If we assume then that the relations connecting w and t, and Ω and t, are known the problem is solved.

Let
$$\frac{dw}{dt} = F(t), \qquad \frac{d\Omega}{dt} = G(t),$$

$$\Omega = \log \zeta = \log (dz/dw), \text{ when } Q = 1.$$

* Forsyth, 'Theory of Functions,' § 267 (1900).

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$$\Omega = \int G(t) dt.$$

Therefore

$$\zeta = e^{\int G(t)Qdt}$$
, i.e. $dz/dw = e^{\int G(t)dt}$.

Therefore

$$dz/dt = e^{\int G(t)dt} F(t),$$

which gives a relation between the length of the plane and t.

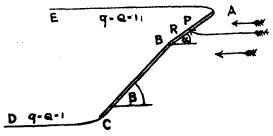
For the thrust we have $\int p \left| \frac{dz}{dt} \right| dt$, taken over the front and back of the plane, so that if the density of the fluid be ρ , the thrust is

$$\frac{\rho}{2} \int (1-q^3) \left| \frac{dz}{dt} \right| dt, \quad \text{when } Q = 1.$$

§ 2. The Theory of Discontinuous Motion Applied to a Bent Plane.

After having given a list of the functions employed, we proceed to use them to find the thrust on a bent lamina.

Let ABC be a section of the lamina, the relative motion of the fluid being denoted by the arrows (fig. 1). Let α and β be the angles AB and BC respectively make with the direction of the fluid at infinity. Let P be the point at which the stream divides.



F10. 1.

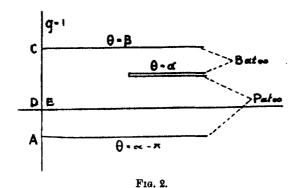
The velocity vanishes at P. The velocity also vanishes at the bend B,* and must therefore have a maximum at some point R in BP.

Let Q = 1 (until § 6), then

$$\Omega = \log(1/q) + i\theta.$$

If $\theta = \alpha$ along PB, $\theta = \beta$ along BC and $\alpha - \pi$ along PA, At D and E q = 1 and $\theta = 0$, and q = 0 at P and B. Consequently the Ω diagram is as shown in fig. 2.

^{*} Lamb, 'Hydrodynamics' \S 63 (1906). The angle ABC (above, fig. 1) $<\pi$.



 $w = \phi + i\psi$ is represented in fig. 3, and we assume the integration constants so chosen that w = 0 at P.

Finally, with $t-p=\sqrt{w}$, we obtain the t diagram, as given in fig. 4.

The Schwarz-Christoffel formula is now applied to transform the Ω diagram to the t diagram. In this case it is

$$\frac{d\Omega}{dt} = \frac{\text{const.}(t-r)}{(t-b)(t-p)\sqrt{(t-a)(t-c)}},$$

where t = r, b, p, a, and c are the values of t at R, B, P, A, and C respectively.

Splitting up by partial fractions and putting y = 1/(t-b) in one case, and = 1/(t-p) in the other, and integrating we have

$$\Omega = A_1 \log \frac{\sqrt{(t-a)(c-b)} + \sqrt{(t-c)(a-b)}}{\sqrt{(t-b)(c-a)}} + A_2 \log \frac{\sqrt{(t-a)(c-p)} + \sqrt{(t-c)(a-p)}}{\sqrt{(t-p)(c-a)}}.$$
(1)

Referring now to the Ω and t diagrams, figs. 2 and 4, it is evident that as t increases through P, Ω increases through π , and as t increases through B,

 Ω increases through $\beta - \alpha$. Now, calling $\beta - \alpha = \pi/2\nu$ and neglecting the constant factor which occurs throughout, we may write

$$\Omega = 2 \log \frac{\sqrt{(t-a)(c-b)} + \sqrt{(t-c)(a-b)}}{\sqrt{(t-b)(c-a)}} + \frac{1}{\nu} \log \frac{\sqrt{(t-a)(c-b)} + \sqrt{(t-c)(a-b)}}{\sqrt{(t-b)(c-a)}}.$$
(2)

Let us now choose the scale of representation so that c-a=1. Then for c>t>a there is a real angle U between 0 and $\frac{1}{2}\pi$, such that $c-t=\cos^2 U$ and $t-a=\sin^2 U$.*

This gives us

i.
$$w = (t-p)^2 = (\sin^2 U - \sin^2 P)^2 = \sin^2 (U+P) \sin^2 (U-P)$$
. (3)

ii.
$$\sqrt{(t-a)(c-b)} + \sqrt{(t-c)(a-b)} = \sin(U+B)$$
, and so on.

Consequently,

$$\Omega = \log \frac{\sin (U+P)}{\sin (U-P)} + \frac{1}{2\nu} \log \frac{\sin (U+B)}{\sin (U-B)}. \tag{4}$$

The Angles of Attack.—By the term the "angles of attack" we understand the angles the two parts of the bent plane make with the direction of the stream at infinity.

Any particular plane has the following characteristics: P, B, and ν . B depends on the ratio of AB to BC (fig. 1) and ν on the angle between AB and BC. We now proceed to find an expression for P by considering the angles of attack.

AB will be henceforth called the front plane, and BC the rear plane.

$$\Omega = A_1 \log \frac{\sqrt{(t-a)(c-b) + \sqrt{(t-c)(a-b)}}}{\sqrt{(t-b)(c-a)}} + A_2 \log \frac{\sqrt{(t-a)(c-p) + \sqrt{(t-c)(a-p)}}}{\sqrt{(t-p)(c-a)}} = \log \frac{1}{q} + i\theta.$$

First of all, when c > t > b it is evident that, with c > b > p > a, the right-hand side of the above equation is real, therefore

$$\theta = 0$$

This is along the rear plane.

Again, when b > t > p, the part whose coefficient is A_2 is real, whereas the other is imaginary and $= A_1 \log (1/i)$.

Therefore
$$\theta = A_1 \log(1/i) = -A_1 \pi/2$$
.

This is along PB. Finally, p > t > a gives us

$$\theta = (A_1 + A_2) \log (1/i) = -(A_1 + A_2) \pi/2$$

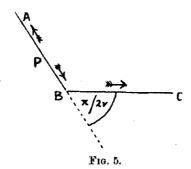
along AP.

* Cf. Greenhill 'The Dynamics of Mechanical Flight."

From fig. 5 we see that if $\theta = 0$ along BC, the values of θ along BP and AP are $-\pi/2\nu$ and $-(\pi + \pi/2\nu)$ respectively, giving

$$A_1 = 1/\nu$$
 and $A_2 = 2$

as before.



Again, for $t = \infty$,

$$\Omega = A_1 \log \frac{\sqrt{(c-b)} + \sqrt{(a-b)}}{\sqrt{(c-a)}} + A_2 \log \frac{\sqrt{(c-p)} + \sqrt{(a-p)}}{\sqrt{(c-a)}}$$

$$= A_1 \log (\cos B + i \sin B) + A_2 \log (\cos P + i \sin P)$$

$$\theta = 2P + B/\nu.$$
(5)

Hence

This, then, is the angle of attack on the rear plane.

We will confine ourselves to positive angles of attack. The angle of attack on the front plane is

$$2P + B/\nu - \pi/2\nu. \tag{6}$$

This is by assumption positive.

Hence
$$2P > \pi/2\nu - B/\nu$$
. (7)

Hence the stream must divide beyond a certain point defined by

$$2P = \frac{1}{2}\pi - B/\nu,$$

which is the limiting position in the case of the front plane being placed parallel to the direction of the stream at infinity.

The Lengths of the Planes.

The lengths of the planes are given by $\int_a^b \left| \frac{dz}{dt} \right| dt$ and $\int_b^c \left| \frac{dz}{dt} \right| dt$. Considering the latter, it can be written in the form $\int_B^{\frac{1}{2}\pi} \left| \frac{dz}{dU} \right| dU$, or, since $\theta = 0$ along the rear plane and z real, in the form $\int_{z_B}^{z_{1\pi}} \left| \frac{dz}{dU} \right| dU$, or, since $\theta = 0$ along the rear U = B and $\frac{1}{2}\pi$ respectively.

Now
$$\zeta = dz/dw$$
, and $w = (\sin^2 U - \sin^2 P)^2$;

therefore

 $L_{2} \text{ (the length of rear plane)} = 4 \int_{B}^{2\pi} \zeta \sin U \cos U \sin (U + P) \sin (U - P) dU.$

Substituting for ζ from (4) $\log \zeta = \Omega$, it is immediately reduced to the form

$$\mathbf{L_2} = 2 \int_{\mathbf{B}}^{\delta \mathbf{w}} \sin^2 \left(\mathbf{U} + \mathbf{P} \right) \sin 2 \mathbf{U} \left\{ \frac{\sin \left(\mathbf{U} + \mathbf{B} \right)}{\sin \left(\mathbf{U} - \mathbf{B} \right)} \right\}^{1/2\nu} d\mathbf{U}. \tag{8}$$

Similarly
$$L_1 = 2 \int_0^B \sin^2(U+P) \sin 2U \left\{ \frac{\sin(B+U)}{\sin(B-U)} \right\}^{1/2\nu} dU$$
, (9) for the front plane.

The Pressures on the Planes.

The pressures are given by

$$\frac{\rho}{2} \int_a^b (1-q^2) \left| \frac{dz}{dt} \right| dt \text{ and } \frac{\rho}{2} \int_b^c (1-q^2) \left| \frac{dz}{dt} \right| dt. \quad \rho = \text{density of fluid.}$$

We first of all proceed to find $\int q^2 \left| \frac{dz}{dt} \right| dt$ for the rear plane. This and the corresponding integrals will be called the Pressure Difference Integrals.

 $\theta = 0$, as before, along the rear plane, hence we write

$$P_2 = \int_{z_B}^{z_B^2} dz = \int \left(\frac{dw}{dz}\right)^2 dz = \int \frac{dw}{\zeta}.$$

Proceeding as in the case of the lengths, we obtain

$$P_{2} = 2 \int_{B}^{4\pi} \sin^{2}(U - P) \sin 2U \left\{ \frac{\sin(U - B)}{\sin(U + B)} \right\}^{1/2\nu} dU, \tag{10}$$

and, similarly,

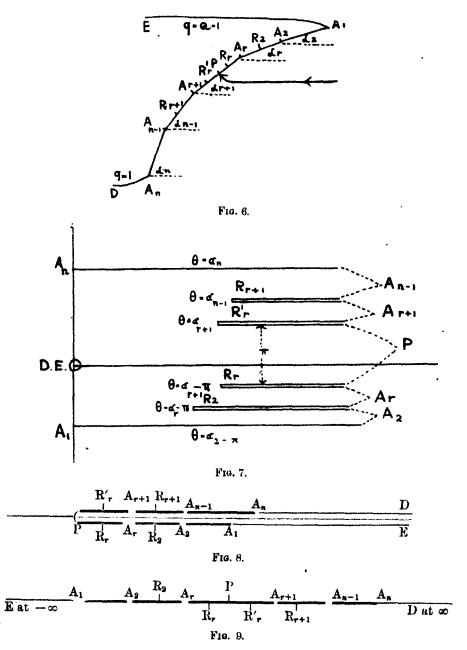
$$P_{1} = 2 \int_{0}^{B} \sin^{2}(U - P) \sin 2U \left\{ \frac{\sin (B - U)}{\sin (B + U)} \right\}^{1/2\nu} dU.$$
 (11)

§ 3. A Further Application to the Case of a Plane with more than One Bend.

Suppose now that we have a plane bent at several points A_2 , A_3 ..., A_r ..., A_{n-1} . Let the angles the parts A_1A_2 , A_2A_r , A_rA_{r+1} ..., $A_{n-1}A_n$, make with the direction of motion of the fluid at infinity be α_2 , α_r , α_{r+1} , ..., α_n respectively.

Let the point P where the stream divides be situated between A_r and A_{r+1} , and the points of maximum velocities be $R_2...$, R_r , R'_r , $R_{r+1}...$, respectively.

 A_1 E and A_n D are the free stream-lines along which q=1 as before The z, Ω , w, and t diagrams are as shown in figs. 6, 7, 8, and 9.



We now apply the Schwarz-Christoffel formula to transform fig. 7 to fig. 9; in this case it takes the form

$$\frac{d\Omega}{dt} = \frac{\text{const.} \left(t - \rho_2\right) \left(t - \rho_r\right) \left(t - \rho_r'\right) \left(t - \rho_{r+1}\right)}{(t - a_2) \left(t - a_r\right) \left(t - p\right) \left(t - a_{r+1}\right) \left(t - a_{n-1}\right) \sqrt{(t - a_1) \left(t - a_n\right)}} \; .$$

 ρ_2 , ρ_r , ρ'_r , ρ_{r+1} correspond to the values of t at R_2 , R_r , R'_r , R_{r+1} , and the a's to the values t corresponding to the A's.

For more bends in the plane additional factors would be inserted in the numerator and denominator of this expression.

Now, putting $\alpha_3 - \alpha_2 = \pi/2\nu_2$, $\alpha_{r+1} - \alpha_r = \pi/2\nu_r$, etc., we have, on splitting up the right-hand side of this equation by means of partial fractions and determining the constants as in the previous case,

$$\frac{d\Omega}{dt} = \frac{\sqrt{(a_{p} - a_{r})(a_{p} - a_{1})}}{(t - a_{p})\sqrt{(t - a_{n})(t - a_{1})}} + \frac{1}{2\nu_{s}} \cdot \frac{\sqrt{(a_{2} - a_{n})(a_{2} - a_{1})}}{(t - a_{2})\sqrt{(t - a_{n})(t - a_{1})}} + \dots
+ \frac{1}{2\nu_{r}} \cdot \frac{\sqrt{(a_{r} - a_{n})(a_{r} - a_{1})}}{(t - a_{r})\sqrt{(t - a_{r})(t - a_{1})}} + \frac{1}{2\nu_{r+1}} \cdot \frac{\sqrt{(a_{r+1} - a_{n})(a_{r+1} - a_{1})}}{(t - a_{r+1})\sqrt{(t - a_{n})(t - a_{1})}} + \dots
+ \frac{1}{2\nu_{n-1}} \cdot \frac{\sqrt{(a_{n-1} - a_{n})(a_{n-1} - a_{1})}}{(t - a_{n-1})\sqrt{(t - a_{n})(t - a_{1})}}.$$
(12)

Integrating as before, and remembering that $\zeta = e^{\Omega}$, we have

$$\zeta = \left\{ \frac{\sqrt{(a_{n} - a_{p})(t - a_{1}) + \sqrt{(a_{1} - a_{p})(t - a_{n})}}}{\sqrt{(a_{n} - a_{1})(t - a_{p})}} \right\}^{2} + \prod_{r=2}^{r=n-1} \left\{ \frac{\sqrt{(a_{n} - a_{r})(t - a_{1}) + \sqrt{(a_{1} - a_{r})(t - a_{n})}}}{\sqrt{(a_{n} - a_{1})(t - a_{r})}} \right\}^{1/\nu_{r}}.$$

To find the angle of attack on the part $A_{n+1}A_n$ (fig. 6), put $t=\infty$ in the equation for Ω (not given here, but obtained from (12) by integration).

$$\Omega = 2 \log \frac{\sqrt{(a_n - u_p)} + \sqrt{(a_1 - a)_p}}{\sqrt{(a_n - u_1)}} + \sum_{r=2}^{r=n-1} \frac{1}{\nu_r} \log \frac{\sqrt{(a_n - a_r)} + \sqrt{(a_1 - a_r)}}{\sqrt{u_{n-1}}}.$$

Now, $a_n > a_{n-1} > ... > a_{r+1} > a_r > ... > a_1$, hence the imaginary part of this expression

$$= i \left\{ 2 \tan^{-1} \sqrt{\left(\frac{a_{p} - a_{1}}{a_{n} - a_{p}}\right) + \sum_{r=2}^{r=n-1} \frac{1}{\nu_{r}} \tan^{-1} \sqrt{\left(\frac{a_{r} - a_{1}}{a_{n} - a_{r}}\right)} \right\}.$$

or using the same artifice as before (3, § 2)

$$= i \left(2 P + \sum_{r=2}^{r=n-1} \frac{1}{\nu_r} U_r \right),\,$$

where U_r is the value of U corresponding to a_r .

Therefore
$$\theta = 2P + \sum_{r=0}^{r=n-1} \frac{1}{\nu_r} U_r$$
 (compare 5, § 2).

 θ is known from the conditions of motion about any particular plane, $U_2, ..., U_{n-1}$ are also known (depending on the points at which the section of the plane is bent); hence P can be determined.

§ 4. Reduction of the Integrals.

When $1/2\nu$ is an exact fraction l/n say, the integrals are reducible to finite form.

Taking, for example, the integral

$$\int_{B}^{\delta\pi} \sin^{2}(U+P) \sin 2U \left\{ \frac{\sin(U+B)}{\sin(U-B)} \right\}^{1/2\nu} dU,$$

$$\frac{\sin(U+B)}{\sin(U-B)} = z^{n},$$

and writing

it will be seen, by expanding the first two factors of the integrand in powers of sin U and cos U, that the integral can be expressed as the sum of integrals of the form

$$\int \sin^p U \cos^q U z^l dU, \quad \text{where } p+q = 4.$$

If we now change the variable from U to z, we have

$$\frac{\tan \mathbf{U}}{\tan \mathbf{B}} = \frac{z^n + 1}{z^n - 1}, \qquad d\mathbf{U} = \frac{-nz^{n-1}\sin 2\mathbf{B} \, dz}{z^{2n} - 2z^n\cos 2\mathbf{B} + 1},$$

$$\cos \mathbf{U} = \frac{(z^n - 1)\cos \mathbf{B}}{\sqrt{(z^{2n} - 2z^n\cos 2\mathbf{B} + 1)}}, \text{ and } \sin \mathbf{U} = \frac{(z^n + 1)\sin \mathbf{B}}{\sqrt{(z^{2n} - 2z^n\cos 2\mathbf{B} + 1)}}.$$

The integrals are all thus reduced to those of rational fractions having as denominator $(z^{2n}-2z^n\cos 2B+1)^3$ and as numerator integral powers of z, and these can easily be integrated by means of partial fractions. While the functions involved have been shown to be "integrable," the results are obviously far too cumbersome to be suitable for the purpose of calculation, and we therefore have recourse to approximate methods of integration.

§ 5. Approximate Evaluation of Integrals.

"Simpson's Rules" will be used to evaluate the integrals where they are applicable, but it is evident that in the neighbourhood of U = B, they fail. The following method will consequently be used near U = B.

Consider
$$\int \sin^2(\mathbf{U} - \mathbf{P}) \sin 2\mathbf{U} \left\{ \frac{\sin(\mathbf{U} - \mathbf{B})}{\sin(\mathbf{U} + \mathbf{B})} \right\}^m d\mathbf{U}.$$

Put U-B=x, and the integrand becomes

$$\sin^m x \frac{\sin^2(x+B-P)\sin 2(x+B)}{\sin^m(x+2B)} = F(x)$$
, say.

When $x \to 0$ (i.e. $U \to B$), $\sin^m x \to x^m$, and we may write $F(x) = x^m \phi(x)$.

 $\phi(x)$ is now expanded in powers of x, being finite and continuous within the limits, and $F(x) = (Ax^m + Bx^{m+1} + Cx^{m+2} + ...) = y$.

Let
$$y_1$$
 be the value of $y = F(x)$ when $x = h$,
 \vdots
 y_r , $x = rh$

Suppose
$$\int_{0}^{rh} y \, dx \text{ (to be required)} = (P_{1}y_{1} + \ldots + P_{r}y_{r}) h$$

$$= (P_{1} + 2^{m}P_{2} + \ldots + r^{m}P_{r}) Ah^{m+1} + (P_{1} + 2^{m+1}P_{2} + \ldots + r^{m+1}P_{r}) Bh^{m+2} + \ldots$$
But
$$\int_{0}^{rh} y \, dx = A (rh)^{m+1} / (m+1) + B (rh)^{m+2} / (m+2) + \ldots$$

Therefore $P_1 + 2$

$$P_1 + 2^m P_2 + 3^m P_3 + ... + r^m P_r = r^{m+1}/(m+1)$$

$$P_1 + 2^{m+1}P_2 + 3^{m+1}P_3 + ... + r^{m+1}P_r = r^{m+2}/(m+2)$$
, and so on.

which, when solved, give the values of P.

In the cases that will be given the lengths and pressures have been calculated for values of m = 1/12, 1/18, 1/36, 1/180, and 0, corresponding to angles $\pi/2\nu = 15^{\circ}$, 10° , 5° , 1° , and 0° between the planes, and r has been taken = 2 giving then

$$P_1 = 2^{m+2}/(m+1)(m+2),$$

$$P_2 = 2m/(m+1)(m+2).$$

The formula here derived, then, will be used in the immediate vicinity of B, from B to B₁ say, on the front plane; $0 < B_1 < B$; and from B to B₂ on the rear plane, $B < B_2 < \frac{1}{2}\pi$. One of Simpson's Rules will be used for the evaluation of the integrals between B₁ and 0, and B₂ and $\frac{1}{2}\pi$, the intervals being 5°.

To test the accuracy of this procedure, the integral $\int_0^a \frac{dx}{\sqrt{(a^2-x^2)}}$ has been evaluated and found to be 1.55, as compared with the true value $\frac{1}{2}\pi = 1.57$. The error is, therefore, about 1.5 per cent. with these intervals.

In applying our rules to the integrals, there are two ways of proceeding.

- (a) Certain fixed values can be given to P and B, P having, of course, to satisfy the condition assigned to it in (7), § 2, and the total lift and drift with the angles of attack determined by these values of P and B found.
- (b) A fixed value can be assigned to B which will determine the ratio of the length of the front to the rear plane, and we have three integrals

$$\int \sin 2 \mathbf{U} \cdot \mathbf{Z}^m d\mathbf{U}, \quad \int \sin^2 2 \mathbf{U} \cdot \mathbf{Z}^m d\mathbf{U}, \quad \int \sin 4 \mathbf{U} \cdot \mathbf{Z}^m d\mathbf{U},$$

to evaluate, with the coefficients $\frac{1}{2}$, $\frac{1}{2}\sin 2P$, and $-\frac{1}{4}\cos 2P$ respectively, for half the lengths of the planes. For $\sin^2(U+P)\sin 2U$ can be written in the form

$$\frac{1}{2}\sin 2U + \frac{1}{2}\sin 2P \cdot \sin^2 2U - \frac{1}{4}\cos 2P \cdot \sin 4U$$
.

[In the pressure difference integrals Z is different, and the sign of P is changed.]

This method has the advantage that after the integrals have been evaluated

we can find the thrusts for any angle of attack, which will determine for us the value of P. One or two cases will be dealt with according to the first method, but the second way will in general, in what follows, be used.

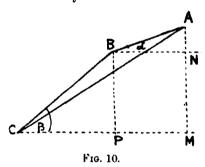
Now, after the lengths of the planes for various values of B have been calculated, they will be reduced in such a way as to make the sum of the semi-lengths equal to 10 c, where c is the circular measure of 5° .

The corresponding lifts and drifts for various angles of attack, and values of m, will accordingly be calculated. Further the thrust on the chord AC (fig. 1, § 2) will be calculated, and results compared.

Finally the lifts and drifts on planes, for different values of B, and the least integral value of P satisfying the condition already cited, will be calculated. This will be done for one value only of m, this being sufficient to give a general conception of the relative advantages of the planes considered.

Calculations have been made for the following values of B; 35° , 40° , 45° , 60° , and 75° , and for the values of m already given. For any other values of B and m the corresponding results can be found by interpolation.

The thrust on the chord is easily obtained as follows:-



BN and CM are parallel to the direction of motion, ANM and BP perpendicular from A and B (fig. 10).

The angles of attack ABN and BCM are α and β respectively.

Let $AB = l_1$ and $BC = l_2$ (which are supposed to be already calculated).

$$AM = AN + NM = l_1 \sin \alpha + l_2 \sin \beta,$$

 $CM = CP + PM = l_1 \cos \alpha + l_2 \cos \beta$.

Therefore the angle of attack ($\zeta = ACM$) on the chord is

$$\tan^{-1}\frac{l_1\sin\alpha+l_2\sin\beta}{l_1\cos\alpha+l_2\cos\beta}.$$

Knowing this, P can be found, and then by means of the method (b) above with m = 0 the thrust can be found.

§ 6. Numerical Results.

The following Tables are given, to illustrate the way in which the general results were obtained.

In the first case (Table I)—

Table 1.

		Front.				Rear.	Sum.	Chord.	
m.	β-a.	a.	$L/ ho c Q^{2}$.	$\mathrm{D}/\rho\sigma\mathrm{Q}^2$.	₿.	$L/ ho c Q^2$. $D/ ho c Q^2$.	L/pcQ2. D/pcQ2.	$\mathbf{L}/ ho c \mathbf{Q}^2$. $\mathbf{D}/ ho c \mathbf{Q}^2$	
1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	15 10 5 1	2½ 5 7½ 9½ 10	1 :688 1 :861 1 :851 1 :216 1 :188	0 ·068 0 ·118 0 ·177 0 ·202 0 ·208	17½ 15 12½ 10½ 10	2 · 280	3 ·868 0 ·770 3 ·273 0 ·680 2 ·919 0 ·523 2 ·484 0 ·485 2 ·876 0 ·416	2 976 0 698 2 778 0 554 2 678 0 530 2 410 0 432 2 380 0 414	

The ratio of the lengths of the two planes has been found in all cases to be approximately independent of m and P. It does not deviate more than 1.5 per cent. from the mean value.

The next Table (II) gives the total lift and drift on a plane in which $B = 75^{\circ}$ for the cases (1) $P = 2^{\circ}$, and (2) when the angle of attack on the front plane is zero. The lift and drift on the chord are also given.

The lengths of the front and rear planes in this case are $8.77 \times 2c$ and $1.23 \times 2c$ respectively.

Table II.

β-α.	Bent plan	ne P = 2°.	Bent plane.	Front attack 0°.	Chord of plane P = 2°		
	$\mathbf{L}/\rho c \mathbf{Q}^2$.	$\mathrm{D}/\rho c\mathrm{Q}^2$,	$\mathbf{L}/ ho c \mathbf{Q}^2$.	$D/\rho\sigma Q^2$.	$L/\rho cQ^2$.	$\mathrm{D}/\rho o \mathrm{Q}^2$	
0	!				1		
15	2 .434	0.150	2 ·111	0.084	0 .958	0.057	
10	1 918	0.113	1 .388	0.086	0.946	0.058	
5	1 '479	0.092	0.687	0.010	0.958	0.062	
1	1 '228	0.080	0 .189	Negligible .	1 '006	0.069	
0	1 '020	0.070	0	ິດີ	1 .020	0.070	

Thirdly, the lift and drift have been calculated for the least integral value of P satisfying the conditions of the problem, and the results given in Table III m = 1/36, $\beta - \alpha = 5^{\circ}$.

В. Р.	P.	$\frac{1}{2c}$ length.		$rac{1}{ ho\sigma \mathbf{Q}^2}$ lift.		$\frac{1}{\rho\sigma Q^2}$ drift.		1 sum of	
	Front.	Rear.	Front.	Rear.	Front.	Rear.	Lift.	Drift	
						1	:		
35	6	1 28	8 .72	0.769	2.088	0 .094	0 448	2 .857	0 .587
40	5	2.01	7 .99	0 .928	1 833	0.116	0 .396	2 756	0.412
45	4	2.78	$7 \cdot 22$	1 .157	1 .894	0.111	0 .286	2 .551	0 867
60	8	5 '84	4 26	1 .655	0 487	0 .125	0.088	2 .182	0 .218
75	2	8.77	1 .28	1 .840	0.139	0.078	0.019	1 .479	0.092

Table III.

Finally in Table IV are given the total lift and drift, and the ratio of lift to drift, for a plane whose angle of attack on its front part is 5°, for values of $B = 35^{\circ}$, 45° , 60° , and 75° , and m = 1/12, 1/18, 1/36, 1/180, and 0.

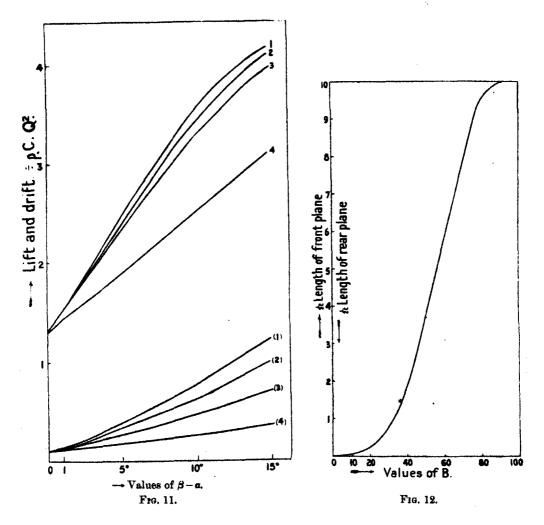
В.	35°.			45°.			6 0°.			75°.		
β-a.	L/pcQ2.	D/pcQ2.	L/D.	$L/\rho cQ^{3}$.	D/pcQ1.	L/D.	L/pcQ2.	$D/\rho\sigma Q^{3}$.	L/D.	$L/\rho cQ^2$.	$\mathrm{D}/ ho o \mathrm{Q}^2$.	L/D.
5 10 5 1 0	4 ·182 3 ·523 2 ·476 1 ·544 1 ·300	1 ·229 0 ·781 0 ·378 0 ·154 0 ·114	3 ·41 4 ·51 6 ·55 10 ·00 11 ·41	4 ·100 8 ·369 2 ·419 1 ·574 1 ·286	1 ·016 0 ·628 0 ·348 0 ·152 0 ·112	4 '03 5 '36 7 '05 10 '36 11 '46	8 ·970 8 ·286 2 ·315 1 ·551 1 ·285	0 ·690 0 ·462 0 ·259 0 ·148 0 ·113	5 ·76 7 ·12 8 ·94 10 ·50 11 ·45	3 ·110 2 ·509 1 ·891 1 ·462 1 ·252	0 ·865 0 ·268 0 ·178 0 ·180 0 ·112	8 · 58 9 · 54 10 · 62 11 · 25 11 · 45

Table IV.

The results contained in this last Table are also given graphically as curves where the lift and drift are plotted against $\beta - \alpha$, fig. 11. The curves 1, 2, 3, and 4 represent the lift for $B = 35^{\circ}$, 45° , 60° , and 75° respectively, while (1), (2), (3), (4) represent the drift.

A curve is also given, in which the length of the front plane is plotted against values of B (fig. 12).

In conclusion we now proceed to examine the above Tables. It is evident that in all cases both the lift and drift are largest when the angle between the planes is largest (for the values of the angle under consideration). This evidently points to the fact that the ratio of lift to the area of the plane is greater, the greater the bend. But the drift is also increased, which is



not desirable in the case of an aeroplane. Again the ratio of lift to drift is greatest when the angle between the planes is least, but the lift is small.

These two conclusions agree with the experimental results that aerofoils with a large camber give a better ratio of lift to surface, whereas nearly flat aerofoils give a better ratio of lift to drift.

The figures given in Table I show, however, that the ratio of lift to drift, for a large value of m even, is greater than the corresponding ratio for the chord, and the lift on a bent plane is much greater than on its chord. Hence it appears that a bent plane is decidedly more efficient than its chord.

Further, from the last Table it is seen that as the length of the front plane increases, the total lift decreases, whereas the ratio of lift to drift increases.

Hence a plane bent near the leading edge gives a better ratio of lift to surface, while on the other hand a plane bent near the rear edge gives a better ratio of lift to drift. Combining these last conclusions with the corresponding ones above, a plane with a large bend close to the front edge gives the best ratio of lift to surface, while a fairly flat plane bent near the rear edge gives the best ratio of lift to drift.

All these conclusions, then, tend to show that a distinct advantage is gained by making use of a cambered plane.

The above methods can be applied to find the thrusts on any bent plane if the ratio of the lengths of its front and rear parts be given. Fig. 12 gives immediately the corresponding value of B. Having been given the angle of attack as well, and the angle at which the plane is bent, P and m are easily found. The case of a plane bent twice can also be considered (as shown in § 3) but the integrals become complicated.

The following application of fig. 12 may, in certain cases, be of use. A glance at fig. 12 shows that between certain limits (viz., between 37° and 75° approximately) the length l of the front plane is a linear function of B = aB + b, say. If, then, the values of B determining the length of the middle part of the plane lie between these limits, we may proceed thus.

Equation 8, § 2, gives in this case

$$z = 2 \int_{B_{1}}^{B_{2}} (U + P) \sin 2 U \left\{ \frac{\sin (U + B_{1})}{\sin (U - B_{1})} \right\}^{1/2\nu_{1}} \left\{ \frac{\sin (B_{2} + U)}{\sin (B_{2} - U)} \right\}^{1/2\nu_{2}} dU$$

$$= \left[aU + b \right]_{B_{1}}^{B_{2}},$$

where $B_2 > U > B_1$, B_1 and B_2 being the two values of B_1 , and ν_1 and ν_2 are the angles of bending at B_1 and B_2 ,

therefore

$$a = 2\sin^2(U+P)\sin 2U \left\{ \frac{\sin(U+B_1)}{\sin(U-B_1)} \right\}^{1/2\nu_1} \left\{ \frac{\sin(B_2+U)}{\sin(B_2-U)} \right\}^{1/2\nu_2},$$

or
$$\left\{ \frac{\sin{(U+B_1)}}{\sin{(U-B_1)}} \right\}^{1/2\nu_1} \left\{ \frac{\sin{(B_2+U)}}{\sin{(B_2-U)}} \right\}^{1/2\nu_2} = \frac{a}{2\sin^2{(U+P)}\sin{2U}},$$

which, when substituted in the formula corresponding to 10, § 2, gives the pressure difference

$$\frac{4}{a}\int_{\mathrm{B}}^{\mathrm{B}_{2}}\sin^{2}(\mathrm{U}+\mathrm{P})\sin^{2}(\mathrm{U}-\mathrm{P})\sin^{2}2\,\mathrm{U}\,d\mathrm{U}.$$

It should be observed that this is not independent of ν_1 and ν_2 , these being included in P. This integral reduces to

$$\frac{4}{a} \int \sin^2 2 \, U \sin^4 U \, dU - \frac{8}{a} \sin^2 P \int \sin^2 2 \, U \sin^2 U \, dU + \frac{4}{a} \sin^4 P \int \sin^2 2 \, U \, dU,$$

the three integrals being easily reducible.*

* Williamson, 'Int. Calc.,' Ch. III.

This method has been tested and found to give results which agree closely with those obtained by the more laborious method applied to the case of the plane with one bend.

The Difference between the Magnetic Diurnal Variations on Ordinary and Quiet Days at Kew Observatory.

By C. CHREE, Sc.D., LL.D., F.R.S.

(Received March 24, 1915.)

§ 1. While investigating the nature of the diurnal inequality of the magnetic elements at Kew Observatory, I have discovered a somewhat remarkable relationship between the inequalities derived respectively from quiet days and from ordinary days (i.e. all days except those of large disturbance). The period whose records were employed consisted of the 11 years 1890 to 1900. During that period five days were selected for each month by the Astronomer Royal as typical of quiet conditions. An analysis of the diurnal inequalities at Kew on these quiet days was given in an earlier paper. Use is also made of the diurnal inequalities at derived from 209 disturbed days, being the days of principal disturbance from 1890 to 1900. The new material employed consists of diurnal inequalities based on all the days of the 11 years, excluding the 209 highly disturbed days but including the quiet days. The cost of measuring the curves was defrayed by a grant from the Government Grant Committee.

The diurnal variation in the horizontal components of magnetic force is often advantageously studied by considering the vector which represents the force to whose action the departure from the mean value for the day may be ascribed.

In the figure NS and WE are perpendicular lines, respectively in and perpendicular to the geographical meridian. If OM and PM, the co-ordinates of the point P, are respectively proportional to the departures of the east and north components of force at any given hour from their mean values for the day, OP represents in magnitude and direction the force to which the diurnal variation in the horizontal plane may be ascribed. The successive positions occupied by P throughout the 24 hours constitute what is known as the vector diagram.

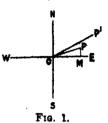
^{* &#}x27;Phil. Trans.,' A, vol. 202, p. 335.

^{† &#}x27;Phil. Trans., A, vol. 210, p. 210.

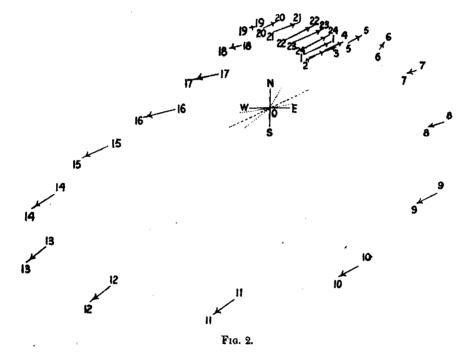
Suppose now that P and P' are corresponding points on the vector diagrams which belong respectively to quiet and to ordinary days, then by

ordinary statics PP' represents in magnitude and direction the force to which may be ascribed the difference between the ordinary day and the quiet day variations.

Fig. 2 shows the variations in PP' throughout the 24 hours, in the case of the mean diurnal inequality for the whole year, as exhibited by the 11 years 1890 to 1900 combined. O is the origin. The arms of the cross, which are oriented N.S. and E.W., each represent



 2γ ($1\gamma \equiv 1 \times 10^{-6}$ C.G.S.). The hours are shown adjacent to the points to which they refer. The arrow in each case is drawn from the point on the quiet day diagram to the point on the ordinary day diagram. To avoid complicating the figure, the vector diagrams themselves are omitted. The



difference vectors answering to 2, 3 and 4 A.M. are partly superposed, so that only one extremity of each line is clearly visible.

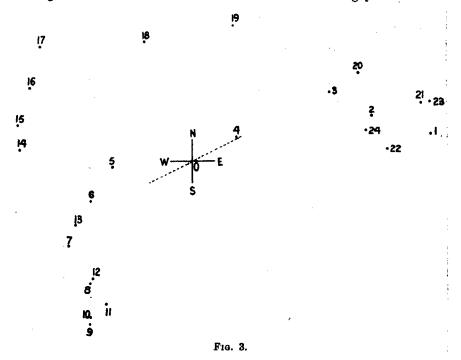
The phenomenon to which I principally call attention is embodied in the fact that the difference vector lines, instead of being oriented promiscuously, show a marked approach to a common direction. The dotted lines through O show the limiting orientations of the difference vector lines. In the S.W.

quadrant the angle between the extreme directions is only 29°. In the N.E. quadrant it is 49°. If, however, we omit 6 A.M., when the difference vector was only 0.7%, the latter angle reduces to 16°. The difference vector vanished between hours 6 and 7, and again between hours 18 and 19 (i.e. 6 and 7 P.M.), and the angles it swung through in these two hours were respectively 133° and 175°. Further, the largest value of the difference vector throughout the 24 hours was only 3.37. In view of these circumstances, the smallness in the variations exhibited by the direction of the vector is truly surprising. The broken line in fig. 2—which is inclined at 64° to the meridian—represents the direction to which the 24 vector difference lines most closely approach. Two calculations were made of its position. The first took simply the arithmetic mean of the inclinations to NS, 180° being subtracted from all angles in the S.W. quadrant; the second weighted the angles according to the magnitude of the difference vector. The results of the two calculations, 63°.96 and 64°.06, agreed so closely that it seemed unnecessary to employ any more mathematically rigid method of calculation. The perpendicular to the broken line, i.e. a line oriented 26° west of north, would practically represent the direction along which the component of the difference vector is a minimum.

§ 2. It is natural to regard the difference between ordinary day and quiet day inequalities as due to the influence of disturbance upon the former. This suggests enquiry into the nature of the difference between disturbed and quiet day inequalities. The necessary calculations had been made in a previous paper,* the results of which are shown graphically in fig. 3. This figure, it should be noticed, is drawn on a different plan from fig. 2. The difference between the disturbed and quiet day vectors is very large, and, owing doubtless in great measure to the small number of disturbed days, the hourly differences are somewhat irregular (to get smooth results thousands of disturbed days would have been required instead of 209).

Thus a diagram constructed on the plan of fig. 2, unless drawn on a very large scale, would have failed to show the results clearly. In fig. 3 lines drawn from 0 to the points marked 1, 2, ..., 24 would represent in magnitude and direction the difference vector (disturbed less quiet day) at hours 1 to 24 respectively, i.e. the lines corresponding to PP' in fig. 2, if P' now lay on the vector diagram for highly disturbed days. The lines have not been actually drawn, as some of them could hardly be shown separately, and the eye can readily supply the deficiency. The broken line represents, as in fig. 2, the inclination of 64° to the meridian. The arms of the cross represent each 2γ .

Fig. 3 admittedly shows much greater variability in the vectorial direction than fig. 2. At the same time there is a remarkable gap between the



direction of the vector at 22 h. (86° east of north) and that at 11 h. (211° east of north). Again, between 4 and 5 h. the vector in vanishing swings through 153°. The vector is included in the N.E. and S.W. quadrants except from 2 to 6 P.M. It is during these afternoon hours that the difference between the phenomena exhibited in figs. 2 and 3 mainly exists. In fig. 2 the vector swung through 175° between 6 and 7 P.M., whereas in fig. 3 it took from 1 to 8 P.M. to swing through 180°. Whether the differences between figs. 2 and 3 would be reduced if an adequate number of highly disturbed days were available it is, of course, impossible to say. At all events the points of resemblance between the two figures are by no means insignificant.

§ 3. Table I gives the data on which figs. 2 and 3 are based, and also the corresponding variations in the vertical force; o-q means ordinary less quiet day vector, and d-q disturbed less quiet day vector. The d-q results, as already indicated, are quoted from a previous paper.

W (CL 14 m)	o	-q Differ	ence vecto	r.	d−q Difference vector.				
Hour (G.M.T.).	φ.	0.	ρ.	R.	ø.	0.	ρ.	R.	
den single grings communication and many fragments in the contract and company dented to			γ	γ	0		γ	7	
1	65	117	8.1	3.5	84	181	21 4	28 4	
2	66	124	8.0	8.6	76	148	16.6	27 .8	
8	69	128	2 ·8	3.6	64	149	13.7	26 4	
4	66	136	2 ·2	8 .2	59	172	3.7	26 1	
5	60	144	1.6	2 .7	266	164	7 -2	26 .	
6	27	161	0.7	2 ·1	249	157	9 '7	25 .	
7	254	159	0.7	2.0	236	144	13 .4	22 8	
8	252	183	1.6	2.2	220	185	14.8	20 1	
9	243	120	2.2	2.6	213	120	17 .2	19 4	
10	242	109	2.4	2 .5	213	107	16 .7	17 1	
11	284	96	2.7	2.7	211	89	15 .0	15 (
12	281	88	2 .6	2.6	221	78	13 .8	14 4	
18	232	81	2 · 4	2 .5	242	50	12.0	15 -1	
14	238	71	2.8	8.0	274	42	15 .2	28 .	
15	245	66	8.1	8 4	282	32	16.0	80 1	
16	256	58	3 .2	3.8	294	26	16.1	87	
17	259	44	2.5	8.6	307	27	17.1	37 .	
18	261	21	1 -2	3.8	388	20	11 4	88 .	
19	76	8	0.4	2.8	17	26	12.6	29	
20	62	29	1 '5	8.1	62	46	17 ·2	28 (
21	69	58	2.6	3 ·2	76	67	21 ·1	22 1	
22	<i>6</i> 1	75	8.3	8.4	86	96	17 .2	17 .6	
28	65	90	3.3	3.3	76	106	21 .8	22 .7	
24	62	105	8.0	3.1	80	132	15 ·8	21 4	
fean from 24 hou			2 · 29	2 99		A	14.9	24.8	
			2 29	2 80	•		14.8	28	
)UTB		2 .31	3.18	•		14.9		
,, night	nours	,	2'81	0.79	•		13.8	25 · 1	

Table I.—Diurnal Inequality. Difference Vector.

 ΔN , ΔE , and ΔV being the north, east, and vertical components of the difference vector, the remaining notation is shown by the equations

$$\rho = \sqrt{(\Delta N^2 + \Delta E^2)}.$$

$$R = \sqrt{(\Delta N^2 + \Delta E^2 + \Delta V^2)}.$$

$$\phi = \tan^{-1}(\Delta E/\Delta N).$$

$$\theta = \tan^{-1}(\rho/\Delta V).$$

R is the resultant difference vector, ρ its horizontal component, ϕ the inclination of ρ to the meridian measured from north to south through east, and θ the inclination of R to the downwardly directed vertical.

The limits to "day" and "night" in Table I are the hours 6 and 18. The fact that the night means of ρ and R actually exceed the day means is remarkable, in view of the large excess of the day means over the night

means in the case of the ordinary vectors, whether for quiet, ordinary, or disturbed days.

The vector is directed above or below ground according as θ is greater or less than 90°. In the case of the o-q vector the time when the vector is below ground nearly coincides with the afternoon.

§ 4. In view of the approach of the horizontal component of the o-q vector to the fixed direction 64° east of north, it seemed desirable to ascertain the variation throughout the 24 hours in its components—say X and Y—along and perpendicular to this direction. It seemed also desirable that these components should be represented in terms of Fourier series with periods 24, 12, etc., hours. The two ends were most readily secured by utilising results already calculated for the horizontal force (H) and declination (D) inequalities.

Representing the o-q difference inequalities in H and D by the series

$$\Delta H = \sum (a_n \cos nt + b_n \sin nt),$$

$$\Delta D = \sum (a_n' \cos nt + b_n' \sin nt),$$

where t represents the equivalent angle (at 15° per hour) to the time elapsed since Greenwich midnight, the component of the horizontal difference vector inclined at any angle ψ to the magnetic meridian (or direction of ΔH) is

$$\sum \{(a_n \cos \psi + a_n' \sin \psi) \cos nt + (b_n \cos \psi + b_n' \sin \psi) \sin nt\}.$$

Here ΔD is supposed to be expressed in terms of 1γ as unit, which means, for the place and epoch considered, writing 5.32γ as the equivalent of 1'.

The mean declination at Kew for the eleven years 1890-1900 was $17\cdot3^{\circ}$ W., so that, to get the component called Y above, we must write $8\cdot7^{\circ}$ for ψ , and similarly for X.

The results finally obtained for X, Y, and the vertical component of the o-q vector, in terms of 1γ as unit, were as follows:—

$$X = 3.32 \sin (t + 80^{\circ}) + 0.41 \sin (2t + 119^{\circ}) + 0.55 \sin (3t + 240^{\circ}) + 0.07 \sin (4t + 49^{\circ}), \quad (1)$$

$$Y = 0.000 \sin (t + 146^{\circ}) + 0.28 \sin (2t + 272^{\circ}) + 0.22 \sin (2t + 272^{\circ})$$

$$Y = 0.09 \sin(t + 146^{\circ}) + 0.28 \sin(2t + 273^{\circ}) + 0.23 \sin(3t + 87^{\circ}) + 0.14 \sin(4t + 158^{\circ}), \quad (2)$$

$$\Delta V = 2.47 \sin(t + 188^{\circ}) + 0.56 \sin(2t + 230^{\circ}) + 0.15 \sin(3t + 293^{\circ}) + 0.04 \sin(4t + 90^{\circ}).$$
 (3)

The fact that Y is insignificant was, of course, implied by fig. 2, but it is interesting to find that the 24-hour term in it is especially insignificant, while the 24-hour term in X dominates all the others. The 24-hour term in ΔV is also largely dominant, so that the o-q difference vector is essentially a phenomenon of a regular kind with a 24-hour period.

Phase angles in cases where the amplitude is very small can hardly claim a very high precision. Thus it may be a pure accident, though a somewhat remarkable one, that the two largest terms in (1) can be written in the form

$$3.32 (\sin \chi + \frac{1}{6} \sin 3\chi)$$

where $\gamma = t + 80^{\circ}$.

Sin χ assumes its extreme values when $t+80^{\circ}$ equals 90° or 270°. This means 40 minutes after midnight and noon respectively.

§ 5. The mean diurnal inequality for the whole year, derived from 11 years combined, may represent a blend of widely divergent characters. In the case alike of the ordinary and quiet days, the diurnal inequality varies much in amplitude and sensibly in type throughout the year. Amplitude and type also vary from year to year with sunspot frequency. It was thus desirable to ascertain whether the phenomenon apparent in fig. 2 varies with the greater or less frequency of sunspots, and whether it holds good of individual months of the year. Attention must first be called to the limitations imposed by the character of the data. The o-q vector is of small amplitude, and any reduction in the number of days utilised must lead to less complete elimination of accidental features. In a single year's results accident might play a dominant part; accordingly, the years of largest sunspot frequency, 1892-1895, were combined in one group, and those of least sunspot frequency-1890, 1899, and 1900-in another group. brevity, these groups will be termed years of sunspot maximum and minimum. The results obtained for the horizontal component of the o-q vector for these two groups of years are given in Table II, the notation being the same as in Table I.

The vector for 19 h. in the sunspot minimum group falls in the S.E. quadrant, but the amplitude being only 0.2γ this has little real significance. If estimates are made of the mean direction of the difference vector in the same way as in the case of the whole 11 years, we get

	From	\mathbf{From}	
	arithmetic mean.	weighted angles.	
Sunspot maximum	63°·4	65°.6	
Sunspot minimum	70°.2	66° 4	

In the case of the sunspot minimum group the vector for 19 h, is nearly perpendicular to the dominant direction. If its angle 153° were replaced in the first calculation by -27° it would reduce the result to 62° 7, while if it were omitted entirely the result would become 66° 6.

The results from the two groups of years are naturally more erratic than those from the 11 years, but in neither case is there any systematic divergence

Table II.—Diurnal Inequality. o-q Difference Vector.

Hour (G.M.T.).	Sunspot maximum.		Sunspot minimum	
110ar (G.m.1.).	φ.	ρ.	φ.	ρ.
		~	6	
1	68	3 ^γ 9	78	2.4
2	67	3.9	76	2 1
8	66	8.6	90	1.7
¥	65	3 · 1	78	1.4
5	78	1 19	66	1.0
6	56	0.4	0	0.7
7	226	1 '0	286	0.7
8	285	2 ·1	274	1.4
9	234	2 ·7	259	1.6
10	242	8.0	246	1 .7
11	240	8 2	245	1.9
12	241	2 -9	225	1.7
18	288	2 .2	219	1.9
14	247	8.8	225	2 .4
15	251	8 4	289	2.6
16	261	3 .7	261	2.4
17	260	2 .9	257	1.7
18	257	1 .8	264	1.0
19	84	0.4	153	0.2
20	58	1.5	63	1.1
21	66	2 .4	68	2.0
22	61	8 . 5	58	2.8
28	70	3.5	62	3.0
24 ,	67	8.8	63	2 .5
Mean from 24 hours		2 .65		1 .75
3 1	8	2.63		1 .74
,, day nour	urs	2 68		1.75

between the angles and those deduced from the complete period. The only conspicuous difference between the sunspot maximum and minimum results is in the amplitude of the difference vector. The excess for the sunspot maximum group is in much the same proportion as in the case of the quiet day vector itself.

§ 6. The N. and W. quiet day inequalities were given in my previous paper only for March, June, and December, in addition to the year as a whole. Also, considering the irregularities in the results for the sunspot minimum year, which depended on 36 months' data, it seemed doubtful whether results depending on only 11 months' data would be satisfactory. It was thus decided to take not the 12 months but the three seasons, winter, equinox (i.e. March, April, September, and October), and summer. Each set of results thus depends on 11 × 4 or 44 individual months.

Fourier coefficients had been calculated in the case of the D and H inequalities for the three seasons, both for ordinary and quiet days. It was thus easy, in the way already illustrated, to obtain the components of the o-q difference vector along any two perpendicular lines in the horizontal plane. The directions selected were 64° east of north and 26° west of north, regarded respectively as axes of x and y.

The following results were obtained:-

Winter-

$$X = 3.03 \sin (t + 82^{\circ}) + 0.44 \sin (2t + 155^{\circ}) + 0.23 \sin (3t + 229^{\circ}) + 0.10 \sin (4t + 204^{\circ}), \quad (4)$$

$$Y = 1.45 \sin (t + 335^{\circ}) + 0.16 \sin (2t + 97^{\circ}) + 0.40 \sin (3t + 129^{\circ}) + 0.10 \sin (4t + 156^{\circ}), \quad (5)$$

Equinox-

$$X = 4.18 \sin (t + 86^{\circ}) + 0.24 \sin (2t + 151^{\circ}) + 0.66 \sin (3t + 226^{\circ}) + 0.28 \sin (4t + 75^{\circ}), \quad (6)$$

$$Y = 0.30 \sin (t + 64^{\circ}) + 0.36 \sin (2t + 275^{\circ}) + 0.38 \sin (3t + 110^{\circ}) + 0.22 \sin (4t + 180^{\circ}), \quad (7)$$

Summer-

$$X = 2.83 \sin (t + 68^{\circ}) + 0.77 \sin (2t + 88^{\circ}) + 0.80 \sin (3t + 255^{\circ}) + 0.16 \sin (4t + 333^{\circ}), \quad (8)$$

$$Y = 1.74 \sin (t + 162^{\circ}) + 0.69 \sin (2t + 274^{\circ}) + 0.41 \sin (3t + 12^{\circ}) + 0.11 \sin (4t + 139^{\circ}).$$
 (9)

In equinox the results are closely analogous to those for the year as a whole; the 24-hour term in X being largely dominant. But in winter and summer, while the 24-hour term in X is considerably the most important term, Y is not negligible compared with X.

The results might mean either that the approach of the difference vector to a dominant direction is much less apparent in the inequalities for winter and summer than in that for the whole year, or that, while there is a dominant direction, it varies with the season. It is easy to decide between the two alternatives.

Suppose $c_n \sin(nt + \alpha)$ and $c_n' \sin(nt + \alpha')$ represent the Fourier waves of a given period in the components of the diurnal inequality along x and y, then the Fourier wave of the same period in the component inclined at an angle ψ to the x-axis has its amplitude C given by

$$C^{2} = \frac{1}{2}(c^{2} + c'^{2}) + \frac{1}{2}(c^{2} - c'^{2})\cos 2\psi + cc'\cos(\alpha - \alpha')\sin 2\psi. \tag{10}$$

The directions making C a maximum or minimum are given by

$$\tan 2\psi = 2\alpha'\cos(\alpha - \alpha')/(c^2 - c'^2). \tag{11}$$

Taking more exact values for a_1 and a_1' than those recorded in (4), (5), (8), and (9), we have for winter

$$c_1 = 3.03\gamma$$
, $c_1' = 1.45\gamma$, $\alpha_1 \sim \alpha_1' = 106^{\circ} 39'$,

for summer

$$c_1 = 2.83 \, \gamma$$
, $c_1' = 1.74 \, \gamma$, $a_1 \sim a_1' = 93^{\circ} \, 27'$.

Whence we find for winter

$$\psi = 170^{\circ} \cdot 2$$

$$C = 3 \cdot 07 \gamma$$
and
$$\begin{cases} \psi = 80^{\circ} \cdot 2 \\ C = 1 \cdot 37 \gamma \end{cases}$$

for summer

$$\psi = 176^{\circ}.6$$
 $C = 2.83\gamma$
and
 $\psi = 86^{\circ}.6$
 $C = 1.74\gamma$

Thus, in both seasons the direction in which the 24-hour term is a maximum departs so little from 64° east of north that the differences between the maximum and minimum values of c_1 and those belonging respectively to X and Y are insignificant.

These results were borne out by an examination of the o-q data for March, June, and December. In March, an equinoctial month, the vector lay in the S.W. quadrant from 8 h. to 18 h. Throughout the rest of the day except at 19 h. it lay in the N.E. quadrant. At 19 h. it lay in the S.E. quadrant, but its amplitude was only 0.8γ .

In June the vector at 5 h. and 6 h. lay in the S.E. quadrant, and from 16 h. to 20 h. it lay in the N.W. quadrant; during the remaining 17 hours it lay either in the N.E. or the S.W. quadrant.

In December the vector lay in the N.E. or S.W. quadrants during 19 hours, but was in the S.E. quadrant at 19 h. and 20 h., and in the N.W. quadrant at 6 h., 7 h., and 8 h.

In both June and December, while the N.E. and S.W. quadrants contained the vector during the greater part of the day, the deviation into the two other quadrants was too decided to be wholly accidental. The afternoon phenomena in June somewhat resembled those in the d-q vector in fig. 3.

§ 7. One remarkable feature remains to be pointed out. The diurnal variation in days of any kind consists not merely of a periodic but also of a non-periodic part, the existence of the latter being evidenced by the non-cyclic change, i.e. the excess of the value at the second midnight over that at the first midnight of the representative day. Thus to complete our information as to the difference between the diurnal variations in ordinary and quiet days, we must consider the relation of the n.c. (non-cyclic) changes.

The apparent n.c. change in any element is composed of several parts. In addition to the secular change, and any true n.c. change characteristic of the

particular type of day, there is in general an instrumental contribution. This may be negligible, and ought at least to be very small in a declination magnetograph; but it may be considerable in a force, especially a vertical force, instrument. In all force instruments there is naturally a drift in one direction, due to change of magnetic moment or of rigidity in the suspension; and unless the magnetograph room has a constant temperature, or temperature compensation is complete, there is a shift of base line value, first in one direction then in the other, due to seasonal change of temperature. In individual days at Kew the apparent n.c. change in V is mainly a question of temperature. If one considers, however, not individual days or months but the whole year—based on as many as 11 years—temperature effects neutralise one another, even in V. Also, while the n.c. changes obtained for the average ordinary or quiet day may owe something to instrumental drift, any such contribution must be practically eliminated when we deal with the difference between the n.c. changes on the average ordinary and quiet days.

The mean n.c. change in ordinary days in D, H and V was found for each of the 132 months. This had been done before for quiet days. The final mean values are

	D.	н.	v.
Quiet day Ordinary day	+ 0·044′ - 0·080′	+ 3 ·84 γ + 0 ·80 γ	-0.84γ -0.42γ
q-o, n.c. change	+ 0.074	+2.547	-0.42γ

The equivalent in force of 0.074' is 0.394 y.

It will be noticed that we have given here the q-o difference, as it happens to be more convenient for our subsequent geometrical work. The o-q difference, of course, differs only in sign. Regarding the q-o n.c. change as a vector quantity, its horizontal component is inclined to the magnetic meridian at the angle

$$\tan^{-1}(0.394/2.54)$$
, or 8.8° .

The magnetic meridian being, as already stated, 17° 3 west of north, the horizontal vector is thus inclined at 26° 1 to the astronomical meridian. In short, it differs by less than the probable error of evaluation from perpendicularity to the line to which the o-q difference inequality vector approaches. Thus what we have found is that the difference between the normal ordinary and quiet day diurnal variations in the horizontal plane consists, to a first approximation, of an oscillation of 24-hour period, along a line inclined 64° to

east of north, and of a change proceeding at a uniform rate throughout the 24 hours along a second line perpendicular to the first.

The resultant of the q-o n.c. changes in D and H has an amplitude of 2.57 γ , its components to north and west being respectively 2.31 γ and 1.13 γ . The resultant of the q-o n.c. changes in D, H and V has an amplitude of 2.60 γ and an inclination of 80°.7 to the upwardly directed vertical.

It is difficult to say whether the ordinary or the quiet day inequality has the greater claim to be regarded as the fundamental. The ordinary days averaged 346 a year, including all but the 209 highly disturbed days of the 11 years, but the inclusion of the omitted days would have had an appreciable The exclusion, moreover, of any particular day was a purely arbitrary matter, except in so far as it was dictated by loss of trace. Some idea of the variability of the days treated as ordinary may be derived from the fact that when "character" figures were assigned to the 11 years, on the international scheme "0" (quiet), "1" (moderately disturbed), "2" (highly disturbed), the average year had 154 days "0," 167 days "1" and 44 days "2." Thus the 346 ordinary days of the average year included 25 (or 7 per cent.) of character "2," while nearly 45 per cent. of them were of character "0." In most months the five selected quiet days were quieter than the average day of character "0," but not conspicuously so. ordinary day inequality, if much more representative, is also of a much more hybrid character than the quiet day inequality.

If we were dealing at one time with the data of, say, 100 years, there would be much to be said for taking as the standard the inequality from all days of the year. But usually what we have to do with at one time are the data of one year, and one really first order disturbance may introduce into the diurnal inequality of the month it occurs in a large element, which can only be regarded as fortuitous, so far as the phenomena of the particular month are concerned. It might, for instance, make a notable difference whether Greenwich or local time was employed in the inequalities.

The main phenomenon of the n.c. change in quiet days at Kew, viz. the large increase in H, has been observed at other places. This suggests the probability that phenomena analogous to those now described may prove to hold good elsewhere. If this should be the case, the fundamental lines to which the phenomena are attached are presumably related in some way to some fundamental direction connected with the earth's magnetism. It is thus a suggestive fact that the vertical plane at Kew inclined at 26° to west of north comes at least near to containing the earth's north magnetic pole.

On the Origin of the "4686" Series.

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[PLATE 3.]

In recent years the class of spectrum lines known generally as the enhanced lines has become of especial importance in connection with their bearing on modern views as to the constitution of the atom. These lines were first investigated by Sir J. N. Lockyer, whose classical researches in this field have shown that a high order of energy is required for their production, and that they are especially conspicuous in many stellar spectra.

An important paper has recently been published by Fowler,* who has shown that the enhanced lines of the elements of the alkaline earth group can be arranged in series similar to those obtained in arc spectra, but that for these series Rydberg's constant N has to be replaced by the value 4N.

In 1896, Pickering† discovered in the spectrum of the star ζ Puppis a series of lines, which from their numerical relationship to the Balmer series were attributed to hydrogen, and which were considered by Rydberg‡ to be the Sharp series of hydrogen, the Balmer series being regarded as the Diffuse series. From the ζ Puppis series, Rydberg calculated the Principal series, the first line of which should have a wave-length of 4688 Å.U., and his conclusions were supported by the fact that a very strong line of about this wave-length was found to occur in the spectra of the nebulæ and certain stars.

Fowler§ subsequently observed the ζ Puppis series, and also a series the first member of which had a wave-length of 4686 Å.U., in vacuum tubes containing helium and hydrogen, which were excited by a strongly condensed electric discharge. Another series was also observed, the first member of which was at $\lambda = 3203$ Å.U., and which converged to the same limit as the 4686 series, being apparently a second Principal series. The three series were approximately represented by the formulæ

^{* &#}x27;Phil. Trans.,' A, vol. 214, p. 225 (1914)

^{† &#}x27;Astrophys. Journ.,' vol. 4, p. 369 (1896); vol. 5, p. 92 (1897).

[†] 'Astrophys. Journ.,' vol. 7, p. 233 (1899).

^{§ &#}x27;Monthly Notices, R.A.S.,' December, 1912.

$$γ Puppis series$$
 $n = N \left\{ \frac{1}{2^2} - \frac{1}{(m+0.5)^2} \right\}, \quad m = 2, 3, 4 ...$
First Principal series
 $n = N \left\{ \frac{1}{1.5^2} - \frac{1}{(m+1)^2} \right\}, \quad m = 1, 2, 3 ...$
Second Principal series
 $n = N \left\{ \frac{1}{1.5^2} - \frac{1}{(m+0.5)^2} \right\}, \quad m = 2, 3, 4 ...$

Fowler was unable to obtain these lines from hydrogen in the absence of helium, but the theoretical investigations of Rydberg appeared to justify the conclusion that the series in question were due to hydrogen.

Bohr* has developed a theory, involving the use of Planck's quantum hypothesis, by which he has arrived at formulæ for the series of lines emitted by an atom of the type investigated by Sir E. Rutherford.† On the assumption that the hydrogen atom consists of a central positive nucleus with a single electron moving around it, Bohr arrived at a formulæ which closely represented the Bahner series. Assuming further that the helium atom consists of a central positive nucleus with two electrons around it, Bohr found that the formulæ obtained closely represented the 4686 and associated series, and by introducing a small correction for the mass of the nucleus, the numerical agreement obtained was remarkably close. Bohr accordingly suggested that the lines in question were due to helium. According to Bohr's theory, the 4686 and 3203 series can be united into one, having a constant 4N instead of N, the correction for the mass of the nucleus involving a modified value of N, and the ζ Puppis lines being alternate members of a 4N series.

The theory has given rise to a considerable amount of theoretical discussion, into which it is not proposed to enter, but it involves the following assumption, with which the present investigation is concerned, namely, that the 4686 and ζ Puppis series owe their origin to helium, and are produced during the binding of an electron by a helium atom, from which two electrons have been removed by the exciting source.

Fowler‡ has come to the conclusion that the series in question are due to helium, from analogy with the 4N series of the alkaline earth metals, and has pointed out that the enhanced lines in general may possibly be explained in this manner, the arc lines being due to the binding of an electron by an atom from which only one electron has been removed.

This view constitutes a wide departure from the earlier hypothesis of the proto-elements, whose mass would probably be some simple fraction of the

^{* &#}x27;Phil. Mag.,' vol. 26, pp. 1, 476, and 857 (1912); vol. 97, p. 506 (1914).

^{† &#}x27;Phil. Mag.,' vol. 21, p. 669 (1911).

¹ Loc. cit., 'Phil. Trans.'

parent atom, whilst the removal of two electrons from an atom would not appreciably affect the mass.

With regard to the origin of the lines, the spectroscopic evidence certainly points to helium. Evans* has observed the 4686 and associated series in vacuum tubes from which the hydrogen had apparently been completely eliminated, and Stark† has also observed the 4686 line in a helium tube showing no trace of the hydrogen lines. This evidence, however, is not conclusive. The extreme difficulty of preparing vacuum tubes free from hydrogen is well known, and the absence of hydrogen lines from the spectrum cannot be taken as conclusive evidence that hydrogen is not present. It is true that 4686 has not been observed in vacuum tubes containing pure hydrogen, but the same may be said of ultra-violet members of the Balmer series, which only appear in hydrogen tubes when helium is also present.‡ In the present investigation an attempt has been made to obtain some evidence of the nature of the atoms concerned in the production of the 4686 series.

The method adopted has been a determination of the highest order of interference of the spectrum lines at which the fringes, produced by the method of Fabry and Perot, remain visible. This depends on the widths of the spectrum lines, a problem which was first treated by Lord Rayleigh, and which has been the subject of quantitative investigation by Michelson. The whole problem has recently been discussed by Lord Rayleigh. It has been shown that the chief cause which determines the breadth of a spectrum line, produced in a gas at low pressure, is the Doppler effect due to the motions of the luminous particles in the line of sight. The limiting order of interference at which fringes may still be visible is given by the relation

$$N = K_{\sqrt{M/T}}$$

where N is the limiting order of interference, K a constant, M the atomic weight of the luminous particle, and T the absolute temperature. The validity of this formula has been experimentally proved by Buisson and Fabry.**

If therefore a source of light, e.g. a vacuum tube, emits a radiation from an atom whose mass is known, it is possible to calculate the mass of an atom

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* 'Nature,' vol. 92, p. 5; 'Phil. Mag.,' vol. 170, p. 284 (1915).
† 'Verh. d. Deutsch. Phys. Ges.,' vol. 16, p. 468 (1914).
‡ Cf. Liveing and Dewar, 'Roy. Soc. Proc.,' vol. 67, p. 467 (1900).
§ 'Phil. Mag.,' vol. 27, p. 298 (1889).
|| 'Phil. Mag.,' vol. 34, p. 280 (1892); 'Astrophys. Journ.,' vol. 3, p. 251 (1896).
¶ 'Phil. Mag.,' vol. 170, p. 274 (1915).
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^{** &#}x27;Journ. de Physique,' vol. 2, p. 442 (1912).

emitting another radiation, from a determination of the limiting orders at which these two radiations show interference fringes. The exact value of the constant K and the temperature T need not be considered. This method of determining the mass of an atom from the breadth of the spectrum lines has recently been applied by Buisson, Fabry, and Bourget* in their remarkable investigation of the Orion nebula. The validity of the formula is restricted to cases in which the radiations are produced in gases at low pressures, since, at higher pressures, broadening of the lines is also caused by disturbances depending on collisions between the luminous particles. Michelson (loc. cit.) has investigated the effect of pressure on the breadth of the lines, and his results show that at pressures as low as one-thousandth of an atmosphere the effect of collisions may be entirely neglected, and at a pressure of 5 mm. of mercury, the broadening due to this cause is still extremely small.

A vacuum tube containing helium and hydrogen at low pressure was excited by an induction coil, with a capacity of 0 0025 microfarad and a spark-gap in the circuit, the spectrum thus obtained consisting of helium lines, hydrogen lines, and 4686.

The pressure in the tube was very low, so that the glass walls fluoresced, the 4686 line appearing only outside the capillary, in accordance with the observations of Fowler.† A convergent beam of light from the vacuum tube was thrown by means of a lens on to the plates of a Fabry and Perot sliding interferometer, and the ring system was focussed by means of an achromatic lens on to the slit of the spectograph, which consisted of a large Hilger constant deviation spectroscope provided with a camera attachment. With this instrument a series of photographs could be taken on the same plate. The experiments were conducted as follows:—

The interferometer plates were set at a small difference of path and a photograph was taken. The difference of path was then successively increased and a series of exposures was made. From the series of photographs thus obtained the limiting order could be estimated. In estimating the limiting order, it will be seen that since on each exposure the order number increases with decreasing wave-length, it is usually possible (if the differences of path have been suitably chosen) to pick out some line in which the fringes are just visible. The determination cannot be made with a high degree of accuracy, but all the photographs taken have yielded concordant results.

In Plate 3, I shows a photograph taken through an étalon giving a

^{* &#}x27;Astrophys. Journ.,' vol. 3, p. 256 (1914).

⁺ Loc. cit., 'Monthly Notices.'

difference of path of 13 mm. It will be seen that the helium lines show sharp rings, whilst the 4686 line and the hydrogen lines show no trace of interference. The plates of this étalon were more heavily silvered than the plates of the interferometer, the fringes being, in consequence, more sharply defined. II shows a series of photographs taken with the interferometer, the differences of path being 2, 4, 12, 16, 20, and 24 mm. The lines at 4471, 4026, and 3889 are much over-exposed, and the fringes are consequently very indistinct. The limits of interference cannot be seen in the reproduction, but on the original plate fringes were just visible in 4686 at $\Delta = 4$ mm., and in helium ($\lambda = 4388$) at 24 mm. (The hydrogen lines are not visible on this plate.)

This gives

$$N_{4686} = \frac{4}{0.0004686}$$
 and $N_{Re} = \frac{24}{0.0004388}$,

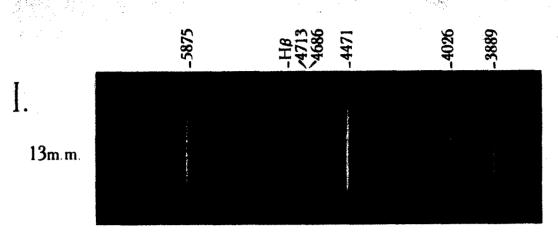
and for the mass of the system from which 4686 originates (He = 4),

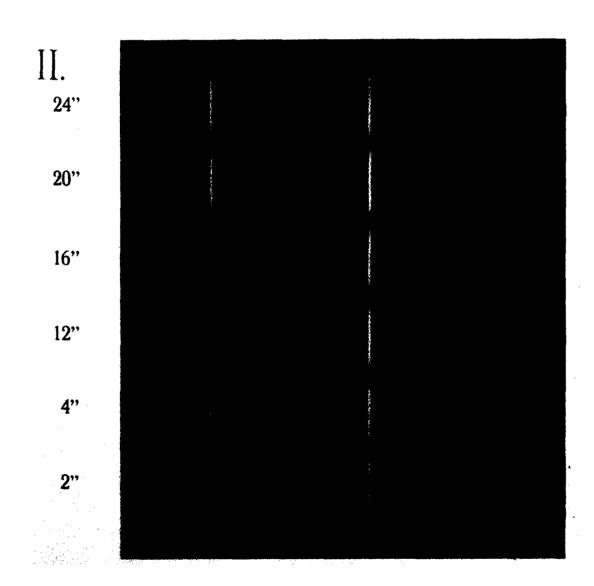
$$4 \times \left(\frac{4 \times 0.0004388}{24 \times 0.0004686}\right)^2 = about 0.094,$$

or about one-tenth of the mass of the hydrogen atom.

It has been pointed out by Lord Rayleigh (loc. cit.) that Michelson's assumption that the temperature of the gas in an electrically excited vacuum tube is not very different from that of the walls of the tube has been amply confirmed by Buisson and Fabry (loc. cit.) in their determination of the change in the value of N when a discharge tube is immersed in liquid air. I have noticed, however, that in the case of the ordinary helium lines the value of N becomes smaller when capacity and a spark-gap are introduced, keeping the current through the primary of the coil unaltered. Buisson and Fabry (loc. cit.) state that under similar conditions broadening occurs in the lines of the Balmer series, but not in the lines of the secondary hydrogen spectrum, and they point out that this would indicate some special cause of broadening for the Balmer series. No mention is made of the pressure in the vacuum tubes at which this observation was made, and at low pressures even a feebly condensed discharge extinguishes the secondary spectrum.

Very little is known with regard to the origin of the secondary spectrum, and the broadening of the Balmer series and of the helium lines may possibly be explained as being due to the sudden rise of temperature at each impulse, but the above calculation might, by analogy, have no significance if the ordinary helium lines corresponded to the secondary hydrogen spectrum. This appears to be unlikely for several reasons. In particular, the solar chromosphere shows the Balmer series and the ordinary helium lines very





strongly, but contains no trace of the secondary hydrogen spectrum. This would indicate that the ordinary helium spectrum and the Balmer series were analogous. On the other hand, however, in such experiments as those of King* the Balmer series behave as enhanced lines, a supposition apparently negatived by Fowler's (*loc. cit.*) demonstration that the Rydberg constant of enhanced series is 4N instead of N.

In any case the observed broadening with a condensed discharge would by itself appear to limit the use of the method employed to cases in which the radiations are produced simultaneously. Thus, in the case of argon, values of N have been found to vary in the red and blue spectra in the ratio of 7.5 to 1, but for the reason given above it is impossible to attach any quantitative meaning to the result. However, in the observations of 4686 and helium the spectra are produced simultaneously. It is possible that this method of calculating the mass of the luminous particles may not be applicable to the enhanced lines, the breadth of which may be controlled by circumstances at present unknown, but if the method is valid in such cases, the results would indicate that the 4686 line is due to systems of subatomic mass.

* 'Astrophys. Journ.,' vol. 38, p. 315 (1913).

Observations on the Fluorescence and Resonance Radiation of Sodium Vapour.—I.

By the Hon. R. J. STRUTT, Sc.D., F.R.S., Professor of Physics, Imperial College, South Kensington.

(Received April 7, 1915.)

§ 1. Experiments on Duration of the Resonance Radiation.

In a paper entitled "Luminous Vapours Distilled from the Arc," I have shown that sodium vapour, stimulated to give the line spectrum by electric discharge, and caused to distil away from the region of discharge, will carry its luminosity with it for a distance of many centimetres. In other words, the luminosity is persistent, and goes on after the electrical stimulation has ceased.

In this case the spectrum emitted is the arc spectrum. It includes not only the D lines, but also the lines of the subordinate series.

We have another method of exciting sodium vapour to emit the line spectrum—I mean fluorescent excitation. If the vapour is illuminated by a soda flame, it will emit the D lines by resonance. It is true that in this case the subordinate series of lines are not excited, but still we should certainly expect at first sight that the D-line radiation would behave as it does with electrical excitation, and that the luminosity would move with the vapour if the latter was rapidly distilled away from the place of excitation.

An important experiment has been described by Dunoyer which seems to show that this is not so. He projected the distilled sodium vapour in a jet across a wide globe; part of the jet was illuminated by a beam of sodium light; and it was found, that when the vapour passed into the shadow it abruptly ceased to be luminous.

It may possibly be objected to Dunoyer's experiment that, since the bulb traversed by sodium vapour was not kept hot, a cloud of condensed sodium may have been formed and that the observed luminosity may have been due to the diffusion of sodium light by this cloud, rather than to genuine resonance radiation.

For this and other reasons it has been thought desirable to repeat Dunoyer's experiment in a modified form, under conditions more closely comparable with those of my own experiments on the electrically excited vapour.

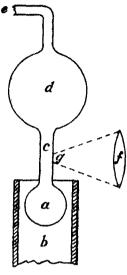
^{* &#}x27;Roy. Soc. Proc.,' A, vol. 90, p. 364 (1914).

^{† &#}x27;Comptes Rendus,' vol. 157, p. 1068 (1913).

Fig. 1 shows the arrangement. The glass bulb a, 4 cm. in diameter, contains a few grammes of dry sodium. It is inserted in b, the chimney of a

small gas furnace, which supplies heat for distilling sodium through the tube c (18 mm. inside diameter) into the cold condensing bulb d, of 9 cm. diameter. It was necessary to prevent condensation in c, and this was achieved by warming it from time to time with a large Bunsen burner held in the hand. The vessel was connected at c to a Gaede molecular pump. A metal diaphragm, backed by a soda flame not too heavily salted,* was focussed on the side of c by means of a short-focus lens, indicated at f. A lantern condenser of 4 inches diameter was generally used, but a cinematograph lens, giving less light but a better defined cone of rays, was sometimes substituted.

The most rapid distillation of the vapour was at the rate of about 15 grm. per hour. In this case the vapour in c was so dense that the resonance radia-



F10. 1.

tion at g was limited to a superficial patch. In other experiments, with less rapid distillation, a cone of luminosity converging to a point could be seen in the vapour.

In neither case was there the slightest indication of the luminosity being carried along with the vapour current. The appearance down stream of the place of excitation was in no way different from the appearance on the up-stream side.

The experiment confirms Dunoyer's conclusion, and emphasises the difference between electrical and fluorescent excitation. In the former case the D luminosity is persistent. In the latter case it is not so.

This will appear still more remarkable and anomalous if we compare the behaviour of sodium emitting the D line with mercury emitting the ultra-violet line at λ 2536. Mercury through which the electric discharge is passing emits this line along with the rest of the arc spectrum, and continues to do so for a time when distilled away from the place of excitation. \ddagger As Wood has shown, mercury vapour can also emit the line λ 2536

^{*} See Dunoyer, 'Journ. de Physique,' January, 1914.

[†] After an experiment sodium can be removed from the vessel by washing it out with alcohol. If the glass has become brown with reduced silicon, it can readily be cleaned by washing with dilute hydrofluoric acid.

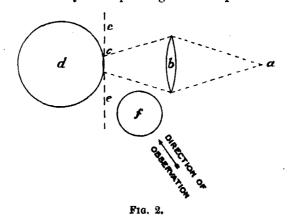
¹ For references, see 'Roy. Soc. Proc.,' A, vol. 91, p. 92 (1914).

without the other mercury lines when light of precisely this wave-length falls upon it. So far the behaviour of mercury and sodium run parallel. Now comes the difference. The luminous centres emitting mercury resonance radiation of wave-length 2536 can be distilled away from the place of excitation as well and easily as if they had been excited electrically.* The centres emitting the resonance radiation of sodium cannot, as we have seen, be distilled away from the place of excitation at all.

I cannot at present make any suggestion as to how these facts should be regarded. It seems very strange that the analogy between the behaviour of sodium and mercury should go so far, and then suddenly break down.

§ 2. Invisibility of the Resonance Radiation through Dilute Sodium Vapour.

Dunoyer's improved methods of observing the resonance radiation of sodium have already been referred to. He noticed that when a soda flame a, fig. 2, is focussed by a lens b on to the wall of a bulb d containing sodium vapour at a density corresponding to a temperature of, say, 300° C.,



the resonance radiation did not penetrate into the depth of the vapour but was confined to a very thin layer at c. The light from this layer of superficial resonance could be seen from any direction in front of the plane ee, but from any direction behind this plane (looking through the bulb) was invisible.

Dunoyer suggests that this may be explained simply by the opacity of the vapour for the particular radiation, though he apparently had some alternative

* See F. S. Phillips, 'Roy. Soc. Proc.,' A, vol. 89, p. 39 (1914). The rate of distillation of mercury used by Phillips was only about twice as great as the rate of my most rapid sodium distillation, measuring the rate in each case by the number of molecules passing per second.

explanation in mind. The absorption is, however, a sufficient explanation, as is proved by the simple experiment illustrated in fig. 2.

The spot of resonance radiation was viewed through a second exhausted bulb f containing sodium. This bulb was heated, and as the temperature rose the resonance radiation appeared dimmer, finally becoming invisible. The temperature at which it disappeared was 160° C. as nearly as could be determined. The thickness of the layer of vapour in f was 4.5 cm., but this bulb was not very well exhausted, and it may be that with the sharper absorption band obtained in the pure vapour a less thickness or density of vapour would have sufficed. The bulb f is, of course, at this low vapour density quite transparent to daylight or lamplight, and the inability to see the spot of resonance radiation through it produces so strange an impression that the observer almost feels as if he is being tricked.

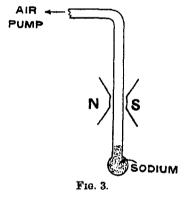
§ 3. Resonance Radiation with the Vapour in a Magnetic Field.

The conical poles of a Dubois half-ring electromagnet were adjusted to a distance of 8 mm. apart, and a glass tube of 4.5 mm. inside diameter was arranged between them as shown in fig. 3. The tube was kept in connection

with a Gaede molecular pump, and, by warming it with a Bunsen burner held in the hand, sodium vapour could be distilled up into the region between the poles. salted flame was focussed on this part of the tube, as in previous experiments.

The effects depend upon how much salt is introduced into the flame. Two kinds of flame have been used.

The first, referred to as the weak flame, was an ordinary Bunsen flame, with a dilute salt solution sprayed into the gas



mixture. This spray was obtained by electrolysis of the dilute salt solution.* The second, referred to as the strong flame, was from a Meker burner, with

abundance of salt melted on to the nickel grid.

Illuminating the sodium vapour with the weak flame, the intensity of the resonance radiation was diminished by exciting the magnet. The stronger the field, the weaker the resonance. With a field of 19,000 units, which was the limit attainable, the resonance was reduced to a very small intensity. It is difficult to say definitely whether it disappeared altogether, since there

* The arrangement is described in 'A Treatise on Practical Light,' by R. S. Clay, p. 507. Macmillan, 1911.

is inevitably some diffusion of soda light by the strike in the glass, and by specks of dust; this diffused light cannot be easily distinguished from the resonance radiation, and remains when the latter is quenched by the magnetic field.

The explanation of this experiment presents no difficulty. The D lines produced by the weak flame are narrow. They were examined visually in the second order of a 10 feet concave grating, and the breadth of D₁ was estimated at 0.2 Ångström, that of D₂ at 0.3 Ångström. D₁ is split by the Zeeman effect into four components, and with the field employed the two inner ones would be separated by 0.41 Ångström.* The component lines of the resonance radiation are so narrow that their breadth may be neglected. All the components of D₁ in the resonance of D₁ would, therefore, be thrown off the exciting line, and the resonance of D₁ would be destroyed. D₂ is split into six components. In a field of 19,000 units the distances of the respective pairs would be about 0.2, 0.6, and 1 Ångström. The two outer pairs, but not the inner pair, would be thrown off the exciting line 0.3 Ångström broad. We see, therefore, that the field should extinguish the whole of the D₁ resonance, and half of the D₂ resonance.† This is in good agreement with the observations.

Using the strong flame instead of the weak one, the effects are more complex. When the full magnetising current is switched on, the resonance radiation is observed to become brighter, to pass through a maximum, and then to diminish again. On switching off, the maximum is passed through again, and then the brightness sinks back to its initial value. These changes each take perhaps two seconds. The magnetic field takes time to reach its full value, and the maximum brightness corresponds to a particular value of the field. This value was determined, though not, of course, very accurately, by diminishing the (steady) magnetising current until, on switching on, the light could not be observed to pass a maximum any longer. This condition was first satisfied when the steady field was about 12,000 units.

To interpret the observations, it is necessary to consider the structure of the D lines in the strong flame. As observed visually in the second order spectrum of the grating, they were seen to be very much broader than the lines emitted by the weak flame.

The breadth of D_1 was estimated at 0.8 Ångström, and of D_2 as 1.1 Ångström. Further, the lines showed extremely distinct reversals. The breadth of the relatively dark centre of the line was perhaps in each

^{*} See Runge and Paschen, Kayser's 'Handbuch,' vol. 2, p. 670.

[†] The polarisation phenomena indicate that the two outer pairs of D_3 contain only half the total light.

case about a quarter of the total breadth of the line. This would give 0.2 and 0.3 Angströms for D_1 and D_2 respectively.

In the absence of magnetic force the resonating lines fall on the comparatively dark centres of the exciting lines. As the magnetic force increases a resonating line is split into components which fall on to the brighter parts of the exciting line, and the intensity of the resonance increases. A further increase in the field pushes the components of a resonating line beyond the maxima of the exciting line, and the resonance begins to fall off again.

To predict the exact field strength at which the maximum should be attained it would be necessary to know the precise distribution of intensity in each exciting line, as well as the comparative intensity of each Zeeman component of each resonating line. Such data are not available. At the observed optimum field, 12,000 units, the components of D₁ would all be off the dark centre of the exciting line, though well within the limits of the bright part of this line. In the case of D₂ the innermost pair would not be clear of the dark central strip of the exciting line, but the two outer pairs would be on the bright part of this line. Thus the explanation of the maximum which has been given is in good general agreement with the observed breadth and structure of the exciting lines.

To see the resonance clearly pass the maximum it is necessary to use a tube only a few millimetres wide, as described, for the strong field required cannot be produced in a larger vessel. But if it is desired merely to show the increase it is better to use a tube 2 or 3 cm. wide between large flat pole pieces. The light should be limited to a strip 1 cm. wide, along that part of the tube which is in the field. A suitable diaphragm should be placed in front of the flame and focussed upon the tube.

§ 4. Exciting Flame in the Magnetic Field.

The flames used were as before, and either of them could be placed between large flat polerpieces, allowing of a maximum field of 9000 units. The flame in each case was focussed on the wall of a bulb of 300 c.c. capacity containing sodium. The bulb was kept hot over a gas burner, and was continuously exhausted by the Gaede molecular pump. With the weak flame the resonance was diminished by the field. The experiment serves as a striking demonstration of the Zeeman effect, and of the various experiments described it is perhaps the best for this purpose. Since the vessel containing sodium vapour has not to get into the space between the magnet poles, it can be made large, and a large patch of resonance radiation produced upon it. The effect of the field on this could quite well be shown to 10 or 20 persons at once.

The explanation is, of course, analogous to that already given for the case when the same flame is used, applying the field to the resonating vapour. In the present instance the exciting line is split up and displaced so that the resonating line no longer falls upon it.

The case of the strong flame in the field is less simple. The observed result is that the resonance radiation is increased, though this is not quite so striking as the diminution with the weak flame in the field.

In interpreting this result we have first to consider what effect the field will produce on the broad bright line. Assuming that the Zeeman components are each as broad as the original bright line, the field is insufficient to separate them to any important extent. We have, therefore, still a continuous bright background. On the other hand, the comparatively narrow lines of the reversing layer are definitely separated. Thus they may have uncovered the centre of the bright line, which is the part of it effective in producing resonance. As a matter of fact when the source was examined with the concave grating, it was observed that the dark reversed centre of D₁ became brighter, on exciting the magnet, so that it was now difficult to see that the line was reversed. In the case of D₂ the reversal became broader, though I could not be sure that it was less dark. But the increase in the central intensity of D₁ accounts for the observed increase of resonance radiation.

Both the experiments of this section can readily be made with the volume resonance as well as with the superficial resonance. It is merely necessary to work at a lower temperature.† The effect on the volume resonance is the same as that on the superficial resonance—decrease by magnetising weak flame, increase by magnetising strong flame.

§ 5. Summary.

- 1. The centres emitting resonance radiation of sodium vapour excited by the D lines are not persistent enough to be carried along when the vapour is distilled away from the place of excitation. This result is extraordinary, because it contrasts absolutely with the behaviour of sodium vapour excited electrically. It also contrasts absolutely with the behaviour of mercury vapour, whether excited optically (2536 resonance radiation) or electrically.
- 2. The resonance radiation of sodium cannot be seen through even a very dilute layer of sodium vapour placed in front of it—a layer quite transparent to white light. This explains why the spot of superficial resonance produced

^{*} Of course this discussion of the subject makes no pretensions to completeness.

[†] See Dunoyer, loc. cit.

on the wall of a glass bulb can only be seen from in front, when the light passes to the eye without traversing sodium vapour. From the back it cannot be seen, as Dunoyer has observed.

3. The resonance radiation of sodium vapour is changed in intensity when the vapour is placed in a magnetic field.

If the exciting flame is weakly salted, the radiation diminishes with increasing field strength.

If the exciting flame is strongly salted, the radiation increases to a maximum and then diminishes again.

4. A change in intensity of resonance radiation can also be observed when the exciting flame is placed in the magnetic field.

In this case a weak flame gives diminished radiation in the field, while a strong flame gives increased radiation in the field.

5. All the facts summarised under 3 and 4 can be explained qualitatively and quantitatively, so far as the available data will go, by taking into account the known Zeeman resolution of the D lines, and the observed width and structure of these lines as emitted by the flames used. The latter data were obtained by observation with a concave grating of high resolution.

I have much pleasure in thanking Prof. A. Fowler, F.R.S., and Mr. F. S. Phillips for help in making these observations with the grating.

The Absorption in Lead of the γ -Rays emitted by Radium B and Radium C.

By H. RICHARDSON, M.Sc., Demonstrator in Physics, School of Technology,

Manchester.

(Communicated by Sir Ernest Rutherford, F.R.S. Received April 3, 1915.)

In a previous paper by Rutherford* and the author attention has been drawn to the fact that the two types of y-radiation emitted by radium B and radium C which are exponentially absorbed by aluminium both show irregular absorption curves when lead is used as the absorbing material. The curve obtained for pure radium C was observed to fall far more rapidly than was to be expected from an exponential law of absorption, and was found to become exponential only after traversing a thickness of 1.5 cm. of The absorption curve in lead of the y-rays from radium B was obtained by taking the difference between the radium (B+C) and the radium C curves. The results so obtained were not determined with very great accuracy, but they served to show that in this case, too, the absorption is not exponential, and that the absorption coefficient rapidly diminished from about $\mu = 11 \, (\text{cm.}^{-1})$ to $\mu = 2 \, (\text{cm.}^{-1})$. The accuracy of the curves did not, however, permit of their complete analysis as in the case of those previously obtained for aluminium.

During the course of his work on characteristic radiations Barkla† has pointed out and investigated the anomalous effect on the absorption of a characteristic radiation by an element whose atomic weight is near to that of the element which emits the radiation. His experiments were, however, confined to elements of comparatively low atomic weight. As the atomic weights of radium B and radium C can only differ by a small amount, and as they have atomic numbers‡ differing only by unity, viz., radium B = 82 and radium C = 83, it seemed of importance to determine accurately the absorption curves in lead, and to examine whether any additional information can be obtained which may indicate whether the radiations emitted by radium B and radium C are characteristic of these elements and fall into the series given by Barkla.

Method of Experiment.—It has been pointed out that the absorption curve for the radium B radiation was previously obtained as a difference curve by

^{*} Rutherford and Richardson, 'Phil. Mag.,' vol. 25, p. 722 (1913).

[†] Barkla, 'Phil. Mag.,' vol. 22, p. 396 (1911).

[‡] Rutherford and Andrade, 'Phil. Mag.,' vol. 27, p. 854 (1914).

finding first of all the curve using an a-ray tube as the active source, and by allowing for the effect due to the radium C. In order to obtain direct results it was thought better if possible to determine the curve using radium B itself as the source. This is rather difficult owing to the rapid transformation of radium B into radium C. The ideal arrangement was therefore to obtain a source of pure radium B, and then to find several points on the absorption curve whilst the percentage of radium C present In order to do this it was necessary to have a source of pure This was obtained in the following manner: 200 millicuries of radium emanation were enclosed in a glass tube over mercury as shown in fig. 1. The whole was then allowed to remain for a period greater than

four hours so that radioactive equilibrium was established. emanation was then pumped off, and the glass tube was washed with absolute alcohol in order to remove all traces of grease and emanation. By this method one obtains on the glass a deposit of radium A, radium B, and radium C in equilibrium. In order to remove the radium C some nickel filings were placed in the tube, which was then filled with boiling dilute hydrochloric acid. The acid was then kept boiling for about 15 minutes. Experiment* had previously shown that in such a case the radium C is deposited on the nickel, and that the separation is very efficient. It was hoped that by this means the whole of the radium C would be completely removed. Moreover, since the nickel was kept in the solution for 15 minutes



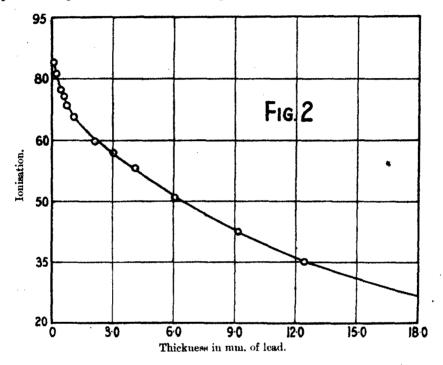
the whole of the radium A had in that time become transformed into radium B, and consequently only pure radium B should remain in solution in the acid. The solution was then quickly poured off on to a quartz plate and evaporated to dryness. The time at which the acid was poured off was noted and in the calculations it was assumed that at that moment only pure radium B existed in the solution. In order to determine how far the assumption was accurate it was only necessary to measure the growth of the radium C by measuring the rise of activity in the ordinary way through a thickness of 1.5 cm. of This can then be compared with the theoretical rise curve as deduced from the theory of successive changes, by assuming the matter to be initially pure radium B. The results of several experiments showed a perfect agreement between the theoretical and actual rise curves and thus justified the assumption that the removal of the radium C by the nickel was quite complete.

In order to determine the absorption curves the apparatus and method already adopted and described in a previous papert was used.

^{*} Rutherford and Richardson, 'Phil. Mag.,' vol. 25, p. 722 (1913).

[†] Rutherford and Richardson, 'Phil. Mag.,' vol. 26, p. 324 (1913).

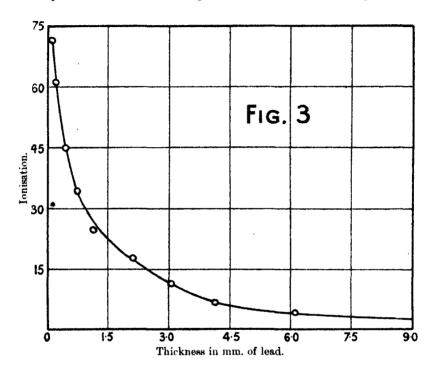
The absorption curve in lead for the radium C radiation was, first of all, carefully determined. For this experiment a source of pure radium C on a nickel wire was used, the soft radiation excited in the nickel being cut out by a very thin sheet of lead. The curve was obtained up to a thickness of 1.8 cm. of lead, after which point the absorption was found to be exponential with an absorption coefficient $\mu = 0.5$ (cm.⁻¹), the value already obtained in previous experiments.* The curve, fig. 2, shows the results obtained.



The radium B absorption curve was next obtained by using the deposit of radium B prepared in the manner already indicated. This curve was, of course, difficult to determine owing to the variation of the amount of radium C present from moment to moment, and also owing to the rapid decay of the radium B itself. The actual curve was obtained in the following manner. The total ionisation was measured for the various thicknesses of lead foil required, in the usual manner. During the course of the experiments several readings were taken of the ionisation through a thickness of 2 cm. of lead, that is, a thickness sufficiently great to cut out entirely the effect due to the radium B. By this means it was possible to calculate the effect due to the radium C present at any time during the experiment, and hence, from fig. 2,

^{*} Rutherford and Richardson, 'Phil. Mag.,' vol. 25, p. 722 (1913).

the effect corresponding to the particular thickness of the absorber being used. The difference between this and the observed ionisation gives the true effect due to the radium B alone. All that is then necessary is to correct the readings for the decay of the radium B itself. In this manner the absorption curve shown in fig. 3 was obtained. This experiment was



repeated several times, the agreement between the separate experiments being very good.

In order to examine whether the absorption curve for the radium B radiation could be accurately obtained by using an α -ray tube as source and allowing for the effect of the radium C, the curve was also again carefully determined. The following Table, which gives the results actually obtained by the two methods, shows that the agreement is well within the limits of experimental error.

Analysis of the Radium B Absorption Curve.—The curves obtained were analysed in the manner already described in previous papers (loc. cit.). The results showed that the radium B radiation consists of three types which are exponentially absorbed. The hardest type has an absorption coefficient $\mu = 1.5$ (cm.⁻¹). The ionisation (measured with an electroscope filled with methyl iodide vapour) due to this type comprises about 12 per cent. of the

Thickness of lead.	Radium B as source.	a-ray tube as source.
mm.		
0 ·1	100	100
0 .2	~85 ·7	82 0
0 4	68 · 1	62 · 7
0.7	47 ·9	47 · 1
1 '09	84 .4	35 .4
2 ·18	26 · 2	22 ·8
8 .06	16 . 5	16 .8
4 15	9.0	10 .8
6 •12	6.2	6.2
9.18	8.5	8.6

Table I.—Absorption in Lead of the y-Rays of Radium B.

total ionisation under the experimental conditions. The two remaining types have coefficients $\mu = 6.0$ (cm.⁻¹) and $\mu = 46$ (cm.⁻¹). About 26 per cent. of the total ionisation is due to the former type of radiation and 62 per cent. to the latter.

Examination of the Radium C Absorption Curve.—Attention has already been drawn to the fact that the absorption curve for the radium C γ -radiation is not exponential from the beginning, but no analysis had so far been attempted. The analysis, performed as in the previous cases, of the curves obtained showed that, under the experimental conditions, about 85 per cent. of the total ionisation produced by radium C is due to the very penetrating type for which $\mu = 0.5$ (cm. $^{-1}$). The absorption curve of the remaining 15 per cent. of the radiation seemed to be very similar in character to that obtained for radium B. The respective curves are shown in fig. 4.

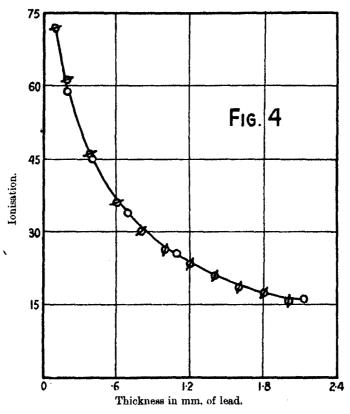
The agreement is well within the errors of experiment and gives conclusive evidence that these radiations are indistinguishable by absorption methods.

Discussion of the Results.—The examination of the absorption curves in lead thus shows that radium B and radium C both emit three types of radiation which are exponentially absorbed, in addition to the very penetrating type of radiation emitted by the latter body. These results are quite in agreement with those recently obtained by Rutherford and Andrade* in their determination of the spectrum of the penetrating γ -rays from radium B and radium C. They concluded that some of the lines in the spectrum were probably close doubles, the lines being considerably wider than would be the case for a radiation of single frequency. The results thus appeared to indicate that part of the spectrum of radium B is not very different from that of radium C. Of course such a small difference of frequency in the radiations as

^{*} Rutherford and Andrade, 'Phil. Mag.,' vol. 28, p. 264 (1914).

indicated by the above experiments would be difficult to detect by the ordinary absorption methods.

It will be observed that the radiations emitted by radium B evidently correspond to that which was previously thought to consist of one single type



O Radium B—absorption curve in lead; φ Radium C—absorption curve in lead (soft type only).

and for which $\mu=0.51$ (cm.⁻¹) in aluminium. Moreover, from the results given previously (loc. cit.), it was assumed that the radiation from radium C consisted of the very penetrating type only, which has the absorption coefficient $\mu=0.115$ (cm.⁻¹) in aluminium. It was, however, pointed out that the presence of a few per cent. of the $\mu=0.51$ type of radiation mixed with the more penetrating type would be very difficult to detect. Owing, however, to the much more rapid absorption of this particular radiation by lead it is easy to demonstrate that it actually does exist.

It should be observed that none of the radiations whose absorption in lead vol. xcl.—A. 2 1

has been investigated correspond with that emitted by radium B* and radium C† and for which $\mu=40~({\rm cm.}^{-1})$ in aluminium. The latter radiation would probably have an absorption coefficient of the order 1000, in lead, and hence would be entirely cut out by the thinnest absorbing layers used in these experiments. The examination of the absorption in lead of this radiation has, not yet been completed on account of the impossibility of obtaining absorbing layers of lead sufficiently uniform and thin.

Characteristic Radiations of Radium B and Radium C.—Evidence has already been given by Rutherford which indicated that the penetrating radiation emitted by radium C might be the K series characteristic radiation of this element. The more recent results of Rutherford and Andrade have, however, led them to conclude that the y-radiation from radium B is the K series characteristic of this element, whilst the very penetrating radium C radiation belongs to some higher series not before observed. It seemed of importance therefore to examine the absorption of these radiations by elements of atomic weight very nearly the same as that of radium C in order to find whether any anomaly in the absorption occurs such as was previously found by Barkla for the elements of low atomic weight. It will be remembered that the absorption coefficient of the radiation characteristic of an element is abnormally high for an absorber of atomic number slightly less than that of the element emitting the radiation. It would appear therefore that if the very penetrating radiation emitted by radium C is the K series characteristic of this element then it should be more readily absorbed in mercury or gold than in lead. It was not found practicable to determine complete absorption curves in the elements of high atomic weight, owing to the difficulty of obtaining large thicknesses of these materials, but comparative values of the absorption coefficients have been determined under the same conditions of experiment. Care was of course taken in every case to cut out all the radium B radiation by inserting a suitable thickness of lead. The results obtained are given in the following Table.

Table II.

Absorber.	Atomic number.	μ/d .
Uranium	92	0 -0475
Lead	82	0 '0435
Mercury	80	0.0416
Gold	79	0.0426
Barium	56	0.0871

^{*} Rutherford and Richardson, 'Phil. Mag.,' vol. 25, p. 722 (1913).

[†] Richardson, 'Roy. Soc. Proc.,' A, vol. 90 (1914).

¹ Rutherford, 'Phil. Mag.,' vol. 24, p. 453 (1912).

It will be seen that no decided change in the absorption coefficient can be detected for the absorbers of different atomic number.

The examination of the absorption curves for the radiation emitted by radium B was then undertaken, the elements uranium, lead, and mercury being taken as absorbers. The absorbing sheets had to be in the form of very thin layers of the oxides, and hence the curves could not be obtained with very great accuracy. Moreover, the actual curves could not be analysed owing to the impossibility, under the experimental conditions, of finding the complete curve for each absorber. The results actually obtained are compared in the following Table:—

Weight per unit area of lead oxide.	Ionisa- tion.	Weight per unit area of uranium oxide.	Ionisa- tion.	Weight per unit area of lead.	Ionisa- tion.	Weight per unit area of mercuric oxide.	Ionisa tion.
grm.	71	grm.		grm.		grm.	
o∵238	100	0 · 2 33	100	0.227	100	o∵226	100
0.461	89 -7	0 458	87 ·2	0 454	87 .5	0.448	87 .8
0 .790	78 9	0.785	75 ·O	0.794	76 ·0	0.806	78 •7
1 .237	72.5	1 .239	69 4	1 .236	70 9	1 .262	69 .4
1 .689	68 .6	1 .705	65 ·9	1 .690	62 4	1 '700	62 0
2.411	63 ·8 ·	2 .404	62 .6	2 415	58 .6	2 .962	51 .4
4 100	54 4	4 109	51 ·9	1		1	
5 .837	49 5	5 348	47.0	1			
6 127	46 7	6 ·183	48 9	1		1 1	
6 . 588	44 6	6 '586	42 .6	1		'	

Table III.

It will be seen from these results that the curves obtained are almost identical, and hence it seems certain that in the case of the radium B radiation, too, no rapid change in the value of the absorption coefficient takes place. If the radiations emitted by radium B and radium C are characteristic of these elements then it would appear that the characteristic radiations of the elements of high atomic weight do not behave as regards absorption in quite the same way as those emitted by elements of lower atomic weight. The direct excitation of the characteristic radiations of the elements of high atomic weight has not, so far, been obtained. If this could be undertaken and the absorption of the radiations then examined the results should give much information on this subject.

Summary.

- 1. The absorption curves in lead of the radiations emitted by radium B and radium C have been determined and analysed.
 - 2. In addition to the penetrating type of radiation for which $\mu = 0.5$ (cm. -1)

in lead, radium C has been found to emit soft types for which $\mu = 46$, $\mu = 6.0$, and $\mu = 1.5$, and which are practically absorbed by 1.5 cm. of lead.

- 3. The analysis of the radium B absorption curve shows that in addition to the radiation $\mu=40$ in aluminium, the rays emitted consist of three types for which $\mu=46$, $\mu=60$, and $\mu=1.5$ for lead. The close similarity of this latter radiation with that of the soft portion emitted by radium C, already observed by Rutherford and Andrade, has been established.
- 4. The absorption of the radiations in different elements has been examined and the bearing of the results discussed. No evidence of anomalous absorption has been found in the case of the penetrating radiations.

I have much pleasure in thanking Sir E. Rutherford for the constant help and valuable advice which he has given me throughout the course of these experiments.

Local Differences of Pressure Near an Obstacle in Oscillating Water.

By Mrs. HERTHA AYRTON.

(Communicated by Lord Rayleigh, O.M., F.R.S. Received February 22, 1915.)

[Plates 4 and 5.]

In a former paper* I showed that when a barrier fits tightly against the sides and across the bottom of a vessel of oscillating water (1) a vortex forms against each side of the barrier in turn as it becomes the lee side; (2) this vortex never forms while the water is attaining to the mean level, but only while it is falling below and rising above that level.

I suggested that such vortices were due to the conjunction of the main stream flowing over the barrier with opposing local streams created by local differences of pressure set up in the neighbourhood of the barrier by the oscillating water. Exception was taken to this explanation, and also, later, to experiments made with a box partially covered with thin gutta percha diaphragms, for the purpose of proving the formation of the local differences of pressure alluded to. The object of the present paper is to give an account of further experiments carried out for this same purpose, with pressure indicators which are free from the objection urged against the diaphragms, viz.: that they themselves might cause variations in the distribution of pressure.

Pressure Indicators.

Fig. 1 shows the form of pressure indicator I now employ, magnified. AB is a glass tube of inner diameter about $\frac{1}{8}$ inch and length about $\frac{3}{8}$ inch, in

which a cork C is fitted, holding a very small glass tube D, through which a stem of graphite passes, carrying two small cork heads E and F. The stem and heads of the plunger EF are so proportioned that the whole either just floats or just fails to float in water, which ensures its moving to and fro through the carrier tube D with the least possible friction, when the whole

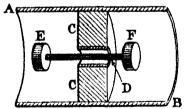


Fig. 1.—Pressure Indicator, Magnified.

pressure indicator is in position in the submerged obstacle. Since D is so small that no current can pass through it, any movement of the submerged

* "The Origin and Growth of Ripple-mark," 'Roy. Soc. Proc.,' A, vol. 84, pp. 290, 291 (1910).

plunger in the direction FE must indicate a greater pressure on F than on E, and in the contrary direction a greater pressure on E than on F.

Method of Using Pressure Indicators.

With these pressure indicators the various differences of pressure set up in oscillating water can be explored, but I shall here confine myself to those which arise close to a submerged obstacle.

In my former paper* each half oscillation, or swing of the water in one direction, was called a swing. The time during which the water approaches the mean level position was called the first part of the swing, and that during which it departs from the level was called the second part of the swing. Using the same terms, the suggestions made on pp. 292-294 as to the differences of pressure set up by the presence of an obstacle in oscillating water may be thus expressed:

- (1) During the first part of any swing the pressure at any point in the lee of a submerged obstacle is less than the pressure at any point—however near it—on its summit.
- (2) During the second part of any swing the above applies still to the upper portion of the lee side, but over the lower portion the case is reversed, and the pressure at any point there is *greater* than the pressure at any point on the summit of the obstacle.

Construction of the Obstacle.

In proving these conclusions by means of pressure indicators, the obstacle used is a block of wood with vertical sides, padded at the ends and underneath to enable it to be pressed tightly against the sides and bottom of the tank, and hollowed out in the part where the pressure indicators are placed. Fig. 2 shows a vertical section in perspective of the hollow portion of the block and of the pressure indicators, EF, which are held in position by tightly fitting bored corks, H, K. The circular hole M, about $\frac{1}{16}$ inch in diameter, is the sole means of communication between the water in the cavity and that outside. Through this hole the pressure of the water passing over the obstacle can be communicated to E_1 , E_2 , the inner heads of the plungers of the pressure indicators, but no oscillation can be set up in the cavity through so small a hole, and only the very small quantity of water that is displaced by the graphite rods in their movements to and fro passes in and out. Great care has to be taken to rid the obstacle and pressure indicators of all air before they are placed in position, as the smallest air

bubble in one of the glass tubes may impede the motion of the plunger. At first the pressure indicators were completely enclosed in the obstacle, all

except the outer edges of their tubes, which were flush with its right-hand side, instead of protruding as in fig. 2. Short lengths of horsehair driven into the heads F_1 , F_2 (fig. 2), parallel to the axes of the tubes, then enabled the movements of the plungers to be observed. As, however, it was found that exactly the same results were obtained when the tubes protruded a quarter of an inch or so beyond the obstacle, the more convenient method shown in fig. 2 was adopted.

The meaning of any movements of the plungers, when the water is oscillated, is quite clear. The only variable pressures acting on the plungers are the pressure at M, transmitted through the water in the cavity to E_1 , E_2 , and the pressures at F_1 , F_2 . If both plungers are pressed outwards it shows that the pressure is greater at M than that either at F_1 or at F_2 ; if both are pressed in,

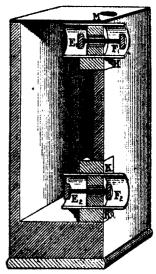


Fig. 2.—Section in Perspective of Obstacle fitted with Pressure Indicators.

the reverse is the case. If one is in and the other out, the pressure at M is less than the external pressure on the first and greater than that on the second.

Fig. 3 (Plate 4) is a photograph of the obstacle with the pressure indicators in position and the water at rest. The obstacle was well to the left of the middle of the trough, the ends of which, as well as the surface of the water, are out of the picture. In order that the direction of flow of the water at various points might be recorded, the three stream indicators made of ravelled silk tipped with cork were used. The one over the obstacle was mounted on a very long headless pin so as to keep it well away from the local disturbances near the obstacle. The one on the floor of the trough close to the obstacle was to the right of the tubular indicator, and the further one was in a line with it. The hole of communication with the cavity marked M in fig. 2 can be seen slightly to the right of the upper tubular indicator. As the indicators are placed, they are evidently in the lee of the obstacle during a swing of the water from left to right, and on its weather side during one from right to left.

Local Differences of Pressure as Shown by Pressure Indicators.

Figs. 4, 5, and 6 are instantaneous photographs taken while the water was being oscillated—fig. 4 during the first part of a swing from left to right, fig. 5 during the second part of one in the same direction, and fig. 6 while the water swung from right to left.

The stream indicators in fig. 4 show that during this first part of a swing the whole of the water was moving from left to right—that close to the lee side of the obstacle as well as that over it and that at some distance away. The plungers of the pressure indicators are both pushed out as far as they will go, showing that the pressure at each of the points F_1 , F_2 (fig. 2), on the lee side of the obstacle was less than that at the point M on top. This is entirely in accordance with the first suggestion made in my former paper and restated on p. 406.

Fig. 5 was taken during the second part of a swing from left to right. The distribution of pressure formerly suggested, and given again on p. 406, is here also justified. For while the upper plunger still remains fully out, the lower is pressed home, showing that during the second part of a swing, although the pressure on the upper part of the lee side of the obstacle remains less than that on top, the pressure on its lower part is greater than that on top. Not only this, however, but the stream indicators point to the fact that while the main stream continued to flow from left to right, there was a current in the opposite direction close to the obstacle; for the stream indicator close to the block has a distinct trend from right to left, although the other two are bent right down in the opposite direction. Here, then, is evidence, not only of the suggested differences of pressure, but also of the fact that the change in the direction of pressure on the lower part of the lee side is the result of no general turning movement on the part of the lower water, but is purely local, and is due to the presence of the obstacle.

Fig. 6 was taken in the course of a swing of the water from right to left, and shows, as was to be expected, that the pressure at any point on the weather side of an obstacle is greater than that at a point on top.

To return to the conditions in the lee of the obstacle. In my paper on "The Origin and Growth of Ripple-mark" I remarked, "the second condition for the formation of a ripple vortex is that the resultant gravity pressure along the ridge on its lee side shall tend upwards." With the obstacle having perfectly vertical sides with which the above experiments were made, there was, of course, no vertical component in the pressure of the water on the sides, but the direction of the vertical component of the pressure of

the water close to the side was easily tested by another experiment. I embedded a pressure indicator in a solid obstacle as shown in section in

fig. 7, and, in order to have a perfectly fair test, I used sometimes a plunger having a slightly greater specific gravity than water and sometimes one with less. result was the same in each case, and was such as was to be expected from the experiments with horizontal indicators—during the first part of a swing from left to right the plunger was pressed downwards, during the second part it was raised. It is clear that these local differences of pressure, in water that would otherwise be at rest in the lee of a barrier, must cause local currents there-downwards during the first part of a swing and upwards during the second. During the first part of a swing, therefore, there is a local pressure difference which creates the condition necessary to give rise to such jets as I have observed by placing a grain of permanganate of potash on the summit of an obstacle.* During the second part of the swing the pressure indicators show that there must be a local current in the lee of the obstacle, somewhere

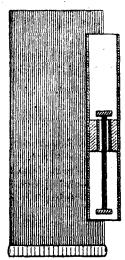


Fig. 7.—Obstacle with Vertical Pressure Indicator for Testing Vertical Pressure.

below the surface, which moves in opposition to the main stream towards the obstacle and upwards. Two currents opposing one another in this way are all that is needed to cause such a vortex as was made manifest in the lee of the obstacle by the grain of permanganate of potash* during the second part of the swing.

Conclusion.

I submit, therefore, that these pressure indicators afford conclusive proof of the truth of the following suggestions, that I first made in 1904, in explanation of the jet and vortex that I had observed in the lee of a submerged obstacle under oscillating water:—

- 1. When the water is approaching the mean level there is a diminution of pressure, or partial vacuum, created in the lee of the obstacle. (Proof in fig. 4.)
- 2. When the water is departing from the mean level the diminution of pressure continues high up on the lee side, but over the lower part there is a pressure in the opposite direction to that of the main stream. (Proof in fig. 5.)

3. The jet in the first part of a swing is due to the local current created by the local difference of pressure; the vortex in the second part of the swing is due to the conjunction of the main stream with the opposing local current set up by the local pressure difference.

My warm thanks are due to Mr. MacKinney for the zeal and ability he displayed in taking the instantaneous photographs from which figs. 3-6 are reproduced.

DESCRIPTION OF PLATES.

Fig. 3.—Obstacle with Pressure and Stream Indicators in Position in Tank, with the Water at rest.

Fig. 4.—Swing from Left to Right-First Part.

Fig. 5.—Swing from Left to Right—Second Part.

Fig. 6 .-- Swing from Right to Left.

Some Problems Illustrating the Forms of Nebula.

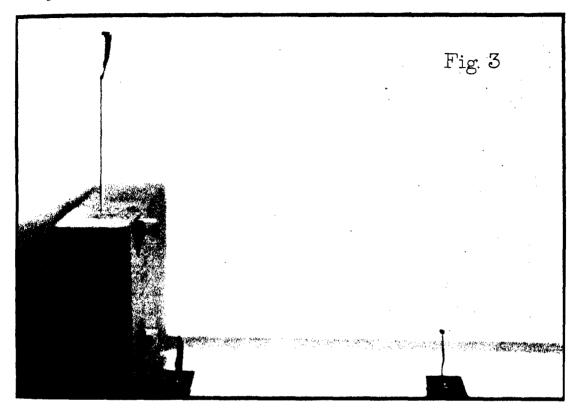
By George W. Walker, A.R.C.Sc., M.A., F.R.S., formerly Fellow of Trinity College, Cambridge.

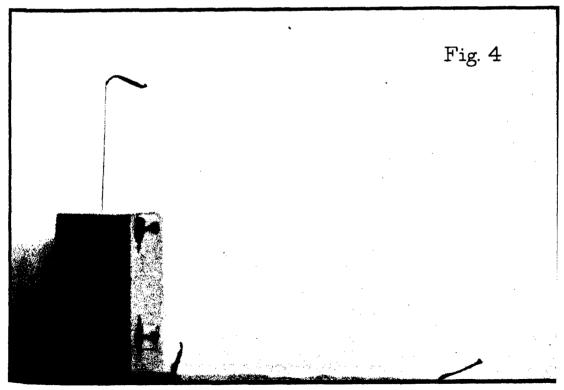
(Received March 27, 1915.)

The possible forms of distribution of a mass of gaseous material under the influence of its own gravitation are of considerable interest in the nebular theory. The law of density which it appears most reasonable to assume is Boyle's Law, in which the pressure is proportional to the density, unless the pressure becomes so great that the material begins to resemble an incompressible substance. Although it is unlikely that the temperature is uniform throughout, still the solution under this restriction would be of value as a step in the direction of greater knowledge as regards possibilities in astronomical phenomena.

The equations can be formed and lead to a differential equation for the surfaces of equal density. This equation is not linear, and in the three-dimensional case little progress to a general solution has been made. In the two-dimensional case, however, considerable progress can be made.

A number of years ago I obtained the exact solution of the statical case of symmetry about the origin. Shortly after I found that Pockels had obtained the complete solution of the statical two-dimensional equation, and







I drew attention to this in a short paper contributed to the 'Boltzmann Jubilee Volume,' p. 242, but, so far as I know, no further application of the solution obtained by Pockels has been made. I have recently examined some particular cases and have arrived at results indicating such a close analogy with actual astronomical forms that I venture to hope they may be of interest as suggesting types that may be expected in three dimensions.

We begin by consideration of the fundamental equations. Let V be the gravitational potential, γ the gravitational constant, p the pressure at any point of the gas, ρ the density at any point of the gas, x, y, the Cartesian co-ordinates of any point.

The hydrostatic equations of equilibrium are

$$\frac{1}{\rho} \left(\frac{\partial \rho}{\partial x}, \frac{\partial \rho}{\partial y} \right) = \left(\frac{\partial \mathbf{V}}{\partial x}, \frac{\partial \mathbf{V}}{\partial y} \right).$$

and the potential must further satisfy the equation

$$\frac{\partial^2 \mathbf{V}}{\partial x^2} + \frac{\partial^2 \mathbf{V}}{\partial y^3} = -4\pi\gamma\rho.$$

If $p = \rho/h$, where h is a constant, we get as an integral

 $1/h \cdot \log \rho = V + \text{constant},$

QI'

$$\rho = \rho_0 e^{h\mathbf{V}}.$$

Hence

$$\frac{\partial^2 \mathbf{V}}{\partial x^2} + \frac{\partial^2 \mathbf{V}}{\partial y^2} = -4\pi \gamma \rho_0 e^{h\mathbf{V}}.$$

This is the equation of which Pockels has obtained the solution in terms of two arbitrary functions as follows. As $\chi = f_1(x+iy) + f_2(x-iy)$ is the solution of $\frac{\partial^2 \chi}{\partial x^2} + \frac{\partial^2 \chi}{\partial x^2} = 0$, then the solution for V and ρ is

$$\rho = \rho_0 e^{h V} = -\frac{1}{2 \pi \gamma h \chi^2} \left\{ \left(\frac{\partial \chi}{\partial x} \right)^2 + \left(\frac{\partial \chi}{\partial y} \right)^2 \right\}.$$

We require to put this in a form which gives real positive values to ρ , and I find that this can be secured by taking

$$\chi = f_1(x+iy) + \frac{1}{f_1(x-iy)}.$$

Otherwise, if ϕ and ψ are conjugate functions, so that

$$\phi + i\psi = f_1(x+iy),$$

we get

$$\chi = \phi + i\psi + \frac{1}{\phi - i\psi},$$

and hence

$$\rho = \rho_0 e^{h\chi} = \frac{2}{\pi \gamma h} \frac{\{(\partial \phi/\partial x)^2 + (\partial \phi/\partial y)^2\}}{(\phi^2 + \psi^2 + 1)^2}.$$

we get

This remarkably general form gives us possible surfaces of equal density, when any known conjugate functions are assigned. I do not know whether a more general form giving real positive density exists, and it may be a matter of interest to pure mathematicians to investigate this point, just as it would be of value to applied mathematicians to know the most general form.

Case I .- If we take

$$\phi = (r/a)^n \cos n\theta, \qquad \psi = (r/a)^n \sin n\theta,$$

$$\rho = \rho_0 e^{hV} = \frac{1}{2} \frac{n^2}{\pi \gamma h a^2} \frac{a^2}{r^2} \operatorname{sech}^2 n \log (r/a)$$

$$= \frac{2n^2}{\pi \gamma h a^2} \frac{a^2}{r^2} \left\{ \left(\frac{r}{a}\right)^n + \left(\frac{a}{r}\right)^n \right\}^{-2}.$$

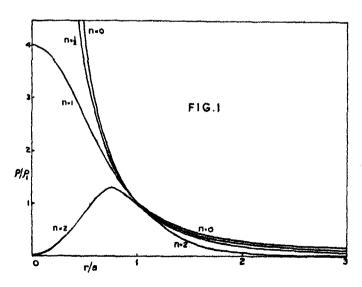
This is the most general case of circular symmetry.

We note that when n < 1 the density becomes infinite at the origin, elsewhere finite, and vanishes at ∞ . When n = 1 the density is finite at the origin, and elsewhere is finite, vanishing at ∞ . When n > 1 the density is zero at the origin, rises to a finite maximum, and then diminishes and vanishes at infinity.

Writing the equation in the form

$$\rho/\rho_1 = 4\frac{a^2}{r^2} \left\{ \left(\frac{r}{a}\right)^n + \left(\frac{a}{r}\right)^n \right\}^{-2}.$$

the curves in fig. 1 show ρ/ρ_1 as a function of r/a, for the four special values $n = 0, \frac{1}{2}, 1$, and 2; α is still at our disposal while $\rho_1 = 2n^2/\pi\gamma h\alpha^2$ is determined when n and α are fixed.



Boyle's Law involves the possibility of an infinite density, and the law does not hold physically so far. In this and in other cases where a singularity occurs we may replace it by a solid nucleus arranged so as to give the proper value of V over its surface.

This case of circular symmetry for n > 1 appears to have some analogy to a ring nebula.

Case II .-- Take

$$\phi = b^{-1} \log r/a, \qquad \psi = b^{-1}\theta,$$

$$\rho = \rho_0 e^{hV} = \frac{2b^2}{\pi N h a^2} \frac{a^2}{r^2} \left[\log^2(r/a) + \theta^2 + b^2 \right]^{-2}.$$

we get

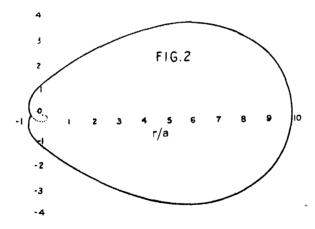
The surfaces of equal density are given by

$$\theta^2 = -\log^2\frac{r}{a} - b^2 + \left(\frac{2b^2}{\pi\gamma ha^2\rho}\right)^{\frac{1}{2}}\frac{a}{r}.$$

The curve, fig. 2, shows the particular surface

$$\theta^2 = -\log^2\frac{r}{a} - 1 + \frac{a}{r},$$

drawn to a scale of 10.



This case is somewhat peculiar. Starting with $\theta = 0$ when r/a = 1, the curve for positive values of θ proceeds as shown, continually approaching the origin by a succession of diminishing spirals. The locus is, however, symmetrical about $\theta = 0$. If now we proceed to draw another surface of different density it would be found to cross the original curve at a succession of points for which $\theta > \pi$. This would mean that at such points two densities are possible, and we cannot admit this. We must, therefore, stop the curve at the nodal point $\theta = \pi$, and then the complete series of curves of equal density form a series of non-intersecting curves of this remarkable

pear shape, the density falling off to zero at infinity and increasing towards the origin with a singularity at the origin itself. The pear may be made sharper or blunter by taking different values of b, which is at our disposal.

This form of distribution is of some interest in connection with the researches of Darwin, Poincaré, and Jeans.

Case III.—Let us take the elliptic co-ordinate transformation

$$x+iy = c \cosh (\xi + i\eta),$$

$$\phi + i\Psi = e^{-\eta(\xi - \xi_0 + i\eta)}.$$

and let

Then we get

$$\rho = \rho_0 e^{hV} = \frac{n^2}{2 \pi \gamma h e^2} (\sin^2 \eta + \sinh^2 \xi)^{-1} \operatorname{sech}^2 n (\xi - \xi_0).$$

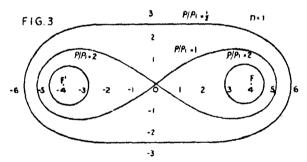
Thus the surfaces of equal density may be written in the form

$$\sin^2 \eta = \frac{\rho_1}{\rho} \frac{1}{\cosh^2 n (\xi - \xi_0)} + 1 - \cosh^2 \xi.$$

For n=1, $\xi_0=0$, we get

$$\sin^2 \eta = \frac{\rho_1}{\rho} \frac{1}{\cosh^2 \xi} + 1 - \cosh^2 \xi.$$

Fig. 3 shows the curves obtained for $\rho/\rho_1 = \frac{1}{2}$, 1, 2. The density falls off to zero towards infinity, while for values $\rho/\rho_1 > 1$ the locus breaks up into



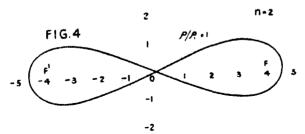
two oval curves about F and F', which are the foci of the original ellipses in the transformation. F and F' are singularities at which ρ would be infinite. The general character of the loci is not altered by giving ξ_0 some finite value. For comparison fig. 4 shows on the same scale the result of putting n=2. The equation is

$$\sin^2 \eta = \frac{\rho_1}{\rho} \frac{1}{\cosh^2 2\xi} + 1 - \cosh^2 \xi,$$

and the curve drawn is for $\rho/\rho_1 = 1$. It is seen to be rather flatter than the corresponding curve for n = 1.

This case then, as a whole, has some analogy in the case of a nebula with two fundamental equal nuclei.

Numerous other cases may be worked out, and it is simply a question of detail in assigning forms to the conjugate functions ϕ and ψ . But perhaps



these three cases are sufficient to indicate the generality of the method, and the remarkable interest of the forms that can be obtained.

I pass to the consideration of an important related problem.

The material of an actual nebula may be moving and not at rest, and in particular it may be rotating. As the rotation, if it exists at all, is very slow, the divergence from the statical equilibrium in such a case would be extremely small, so that the statical solutions are themselves of value. It is, however, of interest to know what the effect of motion may be.

The simplest case we can consider is the final state in which the material rotates about an axis like a rigid body, with steady angular velocity ω . There the problem reduces to a statical one, when we take axes rotating with the material and add to the gravitational forces the centrifugal effect. In the case of a gas such a rotation, however small, can hardly be expected to extend indefinitely, and we should rather expect the motion to fall off and finally cease at a great distance. While keeping this in view, it is not without interest to examine what effect such an imposed uniform rotation would have. Mr. Jeans* has referred to this problem, but without giving details. Some of my results are in agreement with his conclusions and others apparently diverge.

If the components of velocity are u and v, and we neglect viscosity, the equations for a steady motion referred to fixed axes are

$$u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = -\frac{1}{h} \frac{\partial \log \rho}{\partial x} + \frac{\partial V}{\partial x},$$

$$u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} = -\frac{1}{h} \frac{\partial \log \rho}{\partial y} + \frac{\partial V}{\partial y}.$$

$$\frac{\partial}{\partial x} \rho u + \frac{\partial}{\partial y} \rho v = 0.$$

$$\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} = -4\pi\gamma\rho.$$

* 'Phil. Trans.,' vol. 213, p. 462 (1914).

In the case of symmetry, where ρ is a function of r only, we may take

$$u = -yf, v = xf,$$

where f is a function of r only.

The equations then reduce to

$$\rho = \rho_0 e^{h(\nabla + \int f^{a} r dr)},$$

$$\frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial V}{\partial r} = -4 \pi \gamma \rho.$$

If $f = \omega$, we get the case of rigid body rotation, and $\rho = \rho_0 e^{h(V + \frac{1}{2}\omega^2 a^2)}$. If $f = \omega a^2/r^2$, we get an "irrotational" motion, and $\rho = \rho_0 e^{h(V - \frac{1}{2}\omega^2 a^2/r^2)}$.

In the latter case the velocity falls off as r increases but is infinite at the origin. We might make f any function of r; and among these we may select one, e.g. $\omega e^{-r/a}$, which makes the velocity zero at the origin and also zero at great distances. But such cases are not steady and the influence of viscosity would arise.

We cannot, in general, integrate in finite terms the equation

$$\frac{1}{r}\frac{\partial}{\partial r}\frac{\partial \mathbf{V}}{\partial r} = -4\pi\gamma\rho_0 e^{h(\mathbf{V} + \int f^{r}dr)},$$

but if we suppose f so small that V differs from its value V_0 in the statical case f = 0 by a small quantity χ we have approximately

$$r \frac{\partial}{\partial r} r \frac{\partial \chi}{\partial r} = -\frac{2n^2}{\cosh^2 n \log(r/a)} (\chi + \int f^2 r \, dr),$$

while

$$\rho = \frac{1}{2} \frac{n^2}{\pi \gamma h a^2} \frac{a^2}{r^2} \frac{1}{\cosh^2 n \log(r/a)} \{ 1 + h (\chi + \int f^2 r \, dr) \}.$$

Let $\chi + (f^2r dr = z)$, and $r = ae^{\theta}$, then the equation may be transformed to

$$\frac{\partial^2 z}{\partial \theta^2} = -\frac{2n^2}{\cosh^2 n\theta} z + \alpha^2 \frac{\partial}{\partial \theta} e^{2\theta} f^2.$$

Now the equation

$$\frac{\partial^2 z}{\partial \theta^2} + \frac{2 n^2}{\cosh^2 n \theta} z = 0$$

has a solution $z = A \tanh n\theta$.

Hence the equation may be written*

$$\coth n\theta \frac{\partial}{\partial \theta} \tanh^2 n\theta \frac{\partial}{\partial \theta} z \coth n\theta = a^2 \frac{\partial}{\partial \theta} e^{2\theta} f^2,$$

and the particular integral which we require is

$$z = a^2 \tanh n\theta \int \coth^2 n\theta \int \tanh n\theta \frac{\partial}{\partial \theta} f^2 e^{2\theta} d\theta d\theta.$$

* Cf. Boole, 'Differential Equations,' p. 205.

For uniform rotation $f = \omega$, and then

$$z = 2a^2\omega^2 \tanh n\theta \int \coth^2 n\theta \int \tanh n\theta e^{2\theta} d\theta d\theta.$$

In the case n = 1 this gives

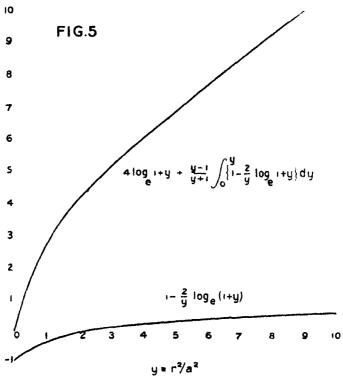
$$z = \frac{a^2 \omega^2}{2} \left\{ 4 \log(y+1) + \frac{(y-1)}{(y+1)} \int^y \left[1 - \frac{2}{y} \log\left(y+1\right) \right] dy \right\},\,$$

and for n=2,

$$z = \frac{a^2 \omega^2}{2} \left\{ 2 \left(\tan^{-1} y - \frac{y}{1 + y^2} \right) + \frac{(y^2 - 1)}{(y^2 + 1)} \int_{-\infty}^{y} \left(1 - \frac{2}{y} \tan^{-1} y \right) dy \right\},$$

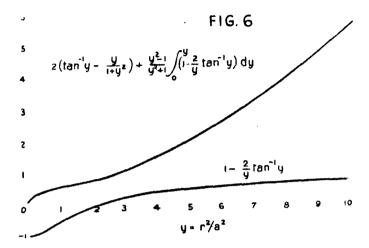
where $y = r^2/a^2$.

These curves are shown to scale in figs. 5 and 6, and we note that in both cases z = 0 when r = 0, is everywhere positive, and finally becomes infinite and proportional to r^2/a^2 when r is great.



The general effect of the rotation is then to increase the density from what would obtain in the statical case, and by increasing proportion as r increases from the origin, but even if it were permissible to pass to large values of τ the density would still diminish to zero. We cannot, however, extend our

solution to large values of z, but we may say that the tendency of the rotation is (e.g. when n=2) to make the density rise more steeply to its maximum



value and to move the point of maximum density further out with increasing ω ; but there is no indication of a tendency to throw off the outer layers. This latter result disagrees with the general conclusion stated by Jeans (loc. cit. ante).

For "irrotational" motion $f = \omega a^2/r^2$ and the particular integral we require is

$$z = \omega^2 a^2 \left\{ \frac{1}{2y} \frac{(3y^2 - 1)}{(y^2 + 1)} + \tan^{-1} y - \frac{(y^2 - 1)}{(y^2 + 1)} \int_y^y \frac{\tan^{-1} y}{y} \, dy \right\} ,$$

where $y = r^2/a^2$.

In this case z is negative and infinite when r=0, rises to a maximum positive value, and again declines to a negative and infinite value as r becomes indefinitely great. As before, we cannot extend our solution to great values of z, but we may say that the tendency of the motion is to make the distribution hollow near the origin, to increase the concentration towards the maximum density at a finite value of r/a and finally to tend to throw off the outer layers when r becomes great. This latter conclusion is in agreement with Jeans.

When we pass to other cases such as Cases II and III, where the original distribution of density is not symmetrical about the origin, it is rather difficult to think of any steady motion other than uniform rotation which would leave the distribution in anything like a permanent form. We must, therefore, confine our attention at present to this case, artificial though it may be.

Taking axes through the origin and rotating with the material with angular velocity ω , we have the equations

$$ho =
ho_0 e^{k(V + \frac{1}{4}\omega^{\gamma,0})},$$
 $rac{\partial^2 V}{\partial x^2} + rac{\partial^2 V}{\partial y^2} = -4\pi\gamma\rho.$

Again, let ω be small and let V differ from its value V_0 when $\omega = 0$ by a small quantity χ . Then

$$\begin{split} \rho &= \rho_0 e^{h\mathbf{V}_0} \left\{ 1 + h \left(\chi + \frac{1}{2} \boldsymbol{\omega}^2 r^2 \right) \right\}, \\ \frac{\partial^2 \chi}{\partial r^2} + \frac{\partial^2 \chi}{\partial u^2} &= -4 \pi \gamma \rho_0 h e^{h\mathbf{V}_0} (\chi + \frac{1}{2} \boldsymbol{\omega}^2 r^2), \end{split}$$

and

or, if $\chi + \frac{1}{2}\omega^2 r^2 = z$,

$$\frac{\partial^2 z}{\partial x^2} + \frac{\partial^2 z}{\partial y^2} = -4 \pi \gamma \rho_0 h e^{h \mathbf{V}_0 z} + 2 \omega^2.$$

In Case II of the distribution of pear-shaped character I find that the solution will have to be obtained by a somewhat complicated series, and as I have not yet gone very far with it I pass to Case III, which can be integrated in finite terms. We had as the statical solution

$$\rho = \rho_0 e^{h\nabla_0} = \frac{n^2}{2\pi\gamma hc^2} (\sin^2\eta + \sinh^2\xi)^{-1} \operatorname{sech}^2 n\xi.$$

Hence the equation we have to solve is

$$\frac{\partial^2 z}{\partial x^2} + \frac{\partial^2 z}{\partial y^2} = -\frac{2n^2}{c^2} z \left(\sin^2 \eta + \sinh^2 \xi\right)^{-1} \operatorname{sech}^2 n \xi + 2\omega^2,$$

or, on changing to elliptic co-ordinates ξ , η , we get

$$\frac{\partial^2 z}{\partial \xi^2} + \frac{\partial^2 z}{\partial \eta^2} = -\frac{2n^2}{\cosh^2 n\xi} z + \omega^2 c^2 (\cosh 2\xi - \cos 2\eta).$$

The solution is $z = z_1 + z_2 \cos 2\eta$, where z_1 and z_2 are functions of ξ only, and satisfy

$$\frac{\partial^2 z_1}{\partial \xi^2} + \frac{2 n^2 z_1}{\cosh^2 n \xi} = \omega^2 c^2 \cosh 2 \xi$$

and

$$\frac{\partial^2 z_2}{\partial \xi^2} - \frac{2 n^2 (2 \cosh^2 n \xi - 1)}{\cosh^2 n \xi} z_2 = -\omega^2 c^2 \qquad \text{respectively.}$$

A solution for z_1 , when $\omega = 0$, is $z_1 = A \tanh n\xi$. Hence the particular integral is

 $z_1 = \omega^2 c^2 \tanh n\xi \int \coth^2 n\xi \int \tanh n\xi \cosh 2\xi d\xi d\xi$

A solution for z_2 , when $\omega = 0$, is $z_2 = A \cosh^2 n\xi$. Hence the particular integral is

$$z_{2} = \frac{\omega^{3}c^{3}}{n^{3}} \left\{ \frac{1}{6} + \frac{1}{3} \cosh^{2} n\xi \log \cosh n\xi - \frac{1}{6} n\xi \tanh n\xi \left(2 \cosh^{2} n\xi + 1 \right)_{i} \right\}.$$

The case n=2 admits of easy expression, and we have

$$\begin{split} z_1 &= \frac{\omega^2 c^2}{4} (\cosh 2\xi - 2 \operatorname{sech} 2\xi) \\ z_2 &= \frac{\omega^2 c^2}{4} \left\{ \frac{1}{6} + \frac{1}{3} \cosh^2 2\xi \log \cosh 2\xi - \frac{1}{3}\xi \tanh 2\xi (2 \cosh^2 2\xi + 1) \right\}. \end{split}$$

We may trace the effect of this on the density. Along the axis of x from 0 to F (see fig. 4) $\xi = 0$, and η changes from $\frac{1}{2}\pi$ to 0.

Hence
$$z = z_1 + z_2 \cos 2\eta = -\frac{1}{4} \omega^2 c^2 (1 - \frac{1}{6} \cos 2\eta),$$
 and so z ranges from $-\frac{7}{24} \omega^2 c^2$ at O to $-\frac{5}{24} \omega^2 c^2$ at F.

From F to ∞ , $\eta = 0$ and ξ ranges from 0 to ∞ . Hence

$$z = z_1 + z_2 = \frac{1}{4}\omega^2 c^2 \left\{ \cosh 2\xi - 2 \operatorname{sech} 2\xi + \frac{1}{6} + \frac{1}{8} \cosh^2 2\xi \log \cosh 2\xi - \frac{1}{6}\xi \tanh 2\xi (2 \cosh^2 2\xi + 1) \right\}$$

This function is $-\frac{\pi}{24}\omega^2c^2$ at F, increases and becomes positive as we increase ξ , and becomes infinite and positive with $\omega^2c^2/4\cosh 2\xi$ as ξ becomes infinite. Again, along the axis of y, $\eta = \frac{1}{2}\pi$, so that

$$z = z_1 - z_2 = \frac{1}{4}\omega^2 c^2 \left\{ \cosh 2\xi - 2 \operatorname{sech} 2\xi - \frac{1}{6} - \frac{1}{6} \cosh^2 2\xi \log \cosh 2\xi + \frac{1}{4}\xi \tanh 2\xi (2 \cosh^2 2\xi + 1) \right\}.$$

At the origin $\xi = 0$ this function is $-\frac{\sigma}{2T}\omega^2c^2$, it increases as ξ increases and becomes positive, finally being infinite and positive with $\frac{1}{4}\omega^2c^2\cosh 2\xi$ as ξ becomes infinite.

The effect of the rotation is then to diminish the density near the origin and to increase it at greater distances, but there is no clear tendency to throw off the outer layers, since the function becomes positive and infinite and not negative and infinite. This is, again, in apparent conflict with Jeans' conclusion. It would thus appear from the cases considered here that a finite boundary of a gaseous mass is not to be looked for as a consequence of rigid body rotation, but rather as a consequence of some other type of motion in which viscosity may play a part.

My sincere thanks are due to Sir Joseph Larmor for kindly criticism and advice.

[Note added April, 1915.—It has been pointed out to me that in Case II $\partial V/\partial \theta$ becomes discontinuous along the line $\theta=\pm\pi$. Hence this is a line of singularities. In accordance with the principle already stated we must, therefore, suppose this line to be occupied by solid matter of the proper density at any point, determined by the change of 1/r. $\partial V/\partial \theta$ in crossing this line. Theoretically this distribution would extend indefinitely, but practically the density of solid matter required at any point on $\theta=\pi$ becomes very small as the distance from the origin increases.]

On the Application of Interference Methods to the Study of the Origin of Certain Spectrum Lines.

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Introductory.

In recent years, great progress has been made in the study of the nature of spectra and of spectral series, but it may be said that very little is yet known as to the nature of the luminous particles from which different spectrum lines originate. It is generally supposed that band spectra are in some way due to molecules, whilst series spectra are usually associated with the atom. Enhanced lines were for many years supposed to be due to proto-elements, or simplified forms of the chemical atom, a view which has recently to some extent fallen into discredit. The evidence for all these hypotheses is of a circumstantial nature, and very little definite evidence as to the nature of the luminous particles is available.

In their recent important researches, Buisson and Fabry* have opened up a new method of attacking the problem. The method adopted by these investigators consists in measuring the limiting order of interference at which fringes can be observed for different radiations. The limiting order of interference depends on the widths of the spectrum lines, from which certain deductions may be made with regard to the temperature of the source of the radiations, and the masses of the particles which are concerned in their production. The theory of the method has recently been discussed by Lord Rayleigh† and by Schönrock.‡ The chief circumstance which need be considered as determining the widths of spectrum lines produced in gases at low pressures is the Doppler effect due to the motion of the luminous particles in the line of sight. The researches of Michelson have shown that at higher pressures a broadening of the lines occurs, this broadening being attributed to disturbances caused by collisions between the luminous particles, but that at pressures below one thousandth of an atmosphere this cause of broadening may be considered negligible.

^{* &#}x27;Journ. de Physique,' vol. 2, p. 442 (1912).

^{† &#}x27;Phil. Mag.,' vol. 170, p. 274 (1915).

^{‡ &#}x27;Ann. der Physik,' vol. 20, p. 995 (1906).

^{§ &#}x27;Phil. Mag.,' vol. 34, p. 280 (1892); 'Astrophys. Journ.,' vol. 3, p. 251 (1896).VOL. XCL.—A.

In the case of radiations produced at low pressures, the limiting order of interference at which fringes may still be visible is given by the relation $N = K \sqrt{(M/T)}$, where N is the limiting order of interference, K a constant, M the atomic weight of the luminous particle, and T the absolute temperature. The value of the constant K is given by Lord Rayleigh (loc. cit.) as 1.427×10^6 , whilst Buisson and Fabry (loc. cit.) adopt the value 1.22×10^6 . In the case of the inert gases, the validity of the formula has been experimentally proved by Buisson and Fabry (loc. cit.), and in the case of sodium by Schönrock (loc. cit.) on the assumption that the radiation originates in the sodium atom. We may now consider more exactly the conclusions which may be drawn from a measurement of the limiting order of interference. If we suppose that at low pressures the only circumstance which can possibly influence the width of the lines is the Doppler effect considered in the theory, it is evident that if the temperature of the source is known, the masses of the luminous particles can be calculated, and conversely, if the masses of the particles be known, the temperature of the source can be determined. In the simple case of two radiations from the same source, if the mass of the luminous particle from which one radiation originates is known, the mass of the luminous particle concerned in the production of the second radiation can be calculated independently of the temperature of the source or the exact value of the constant K.

Any deductions made on the assumption that the only cause of broadening is due to the Doppler effect must be accepted with caution, since there is some reason to suspect that under certain conditions some other cause of broadening may be operative, although such cause of broadening is not at present theoretically indicated. Let us therefore assume that some hypothetical cause of broadening exists. We may write for the breadth Δ of a line, as due to the Doppler effect,

 $\Delta = K_1 \sqrt{(T/M)}.$

Let the breadth of the line as determined by some hitherto unsuspected circumstances be Δ_1 , then the effective breadth of the line which determines the limiting order of interference will be $\Delta + \Delta_1$; whatever circumstances are operative in determining the breadth of a line, the breadth can never be less than Δ , that is to say the value of N found can never be greater than the value indicated by the equation.

It may further be pointed out that any imperfection in the experimental arrangements, any ill adjustment of the interferometer plates, or any deficiency in the technique of observing the indistinct fringes can only give too low a value for N. Any observed value of N may therefore be confidently accepted as an inferior limit. If therefore the mass of the luminous particle is assumed,

a superior limit of the temperature of the source may be calculated with certainty, and conversely, if the temperature of the source is known, an inferior limit for the mass of the luminous particle may be confidently determined.

Experimental.

In the experiments recorded in the present investigation the values of N have been determined in the following manner. A convergent beam of light from the source was thrown by means of a lens on to the plates of a Fabry and Perot sliding interferometer, and the ring systems were focussed by means of an achromatic lens on to the slit of a large Hilger constant deviation spectroscope, each spectrum line thus appearing as a narrow strip of a ring In making visual observations, the interferometer plates were slowly separated until a point was reached at which the fringes were only just visible. From the separation of the plates at this point, the value of N could be calculated. In making photographic observations, the telescope of the spectroscope was replaced by a camera attachment and a series of spectra were photographed on the same plate in juxtaposition, with the interferometer plates set at successively increasing differences of path. The photographic method may be regarded as satisfactory in the determination of the relative values of N for radiations photographed on the same plate, but the author has found that, for radiations which can be sufficiently well seen, visual determinations are greatly to be preferred, especially in the determination of the absolute values of the limiting order of interference.

With regard to the constant K, it is evident that the value must vary somewhat with the observer, the density of the silvering on the interferometer plates, and other circumstances. An observer must, therefore, determine his own value for the constant. I have determined this from a series of observations of the spectra of helium and neon, produced in vacuum tubes with an uncondensed discharge from an induction coil, and the average value of K obtained in this way agrees so closely with the value given by Buisson and Fabry (loc. cit.) that I have adopted their value, $1.22 \times 10^{\circ}$, in the discussion of the results. The arc spectra which have been investigated were produced between carbon poles containing small quantities of the substances under investigation. The arc was maintained in a glass globe of about a litre capacity, which was exhausted by means of a Fleuss pump, and a small mercury gauge attached to the apparatus showed that a pressure of less than 1 mm. of mercury could be maintained. The current consumed varied between 1 and 2 ampères.

Comparison of the g, H, and K Lines of Calcium.

The relative behaviour of these lines has for many years been a subject of investigation, more especially in respect of their appearance in the sun and The q line is a typical flame line, appearing brightly when a calcium salt is volatilised in the Bunsen flame, and also in arc and spark spectra. The H and K lines, on the other hand, are enhanced lines. Whilst scarcely visible in the Bunsen flame, they are well developed in the arc, and in powerful sparks are strongly enhanced relatively to the g line. The H and K lines have recently been shown by Fowler* to be the first pair of a series in which the Rydberg constant "N" is replaced by the value "4N," this type of series being apparently characteristic of enhanced lines. The H and K lines are amongst the most conspicuous of the Fraünhofer lines and the g line is also strong. The former, however, occur at very high altitudes in the chromosphere, where the g line is not visible, and this is also found to be the case in the spectra of many stars. Lorenser has shown that the q line is the first member of a single line Principal series with which Diffuse and Sharp series are also associated.

The observations of these lines were necessarily carried out photographically, and although a considerable number of photographs were taken, the absolute values of N obtained were not satisfactory, though it is believed that the relative values are worthy of some confidence. This is due to a number of circumstances. The unsteady burning and the sudden evolution of denser calcium vapours in the arc are very troublesome in photographic observations, though of much less inconvenience in visual work. The photographic technique is difficult, and a series of spectra on the plate are seldom of the same intensity. The following results were obtained from a number of plates. For the g line, fringes were observed up to a difference of path of 80 mm. Putting $\mathbf{M} = 40$, we get

$$N_{4227} = \frac{80}{0.0004227}$$
 and $\sqrt{(40/T)} \times 1.22 \times 10^{6} = 189259$,

whence $T = 1662^{\circ}$ Abs., a value which would appear to be too low for the temperature of the vacuum are.

The H and K lines are identical in their behaviour. The greatest difference of path at which interference has been observed for the H line was 55 mm. Putting M = 40 as before, we get

$$\sqrt{(40/T)} \times 1.22 \times 10^6 = 138573$$
, and T = 3100° Abs.

It might be supposed that the g line and the H and K lines are produced in

^{* &#}x27;Phil. Trans.,' A, vol. 214, p. 225 (1914).

[†] Dissertation, Tübingen, 1913.

different portions of the arc, but the great difference in temperatures involved would appear to discredit this explanation.

Assuming that all three radiations are produced simultaneously, the relative masses of the luminous particles may be calculated. Thus

$$\frac{\mathbf{M}_{H}}{\mathbf{M}_{g}} = \left(\frac{138573}{189259}\right)^{2} = 0.54,$$

a number suspiciously near and, within the limits of experimental error, equivalent to 1/2. This would indicate that the H and K lines are due to particles having one-half the mass of the particles concerned in the production of the g line.

The simplest explanation would appear to be that the g line, which is essentially a low energy line, is due to calcium molecules Ca₂ of mass 80, the H and K lines being due to calcium atoms of mass 40, which would give a temperature of about 3000° C. as a superior limit for the temperature of the vacuum arc. This view receives strong confirmation from the observations of the flame lines of strontium and barium. The "absolute values" of N for the calcium lines are undoubtedly much too low, so that the value 3000° C. for the temperature is correspondingly too high.

The Flame Lines of Strontium and Barium.

In the spectra of strontium and barium, the lines $\lambda = 4607$ and $\lambda = 5535$ respectively are strictly analogous in their behaviour to the calcium line g. In the case of the strontium line $\lambda = 4607$, Lorenser (*loc. cit.*) has shown that this line is the first member of a Principal series analogous to the series in calcium of which g is the first member.

For $\lambda = 4607$ (Sr) fringes were observed visually up to a difference of path of 183 mm. If a strontium atom were responsible for this radiation, the superior limit for the temperature of the arc would be 834°, clearly an inadmissible value. It is evident that molecules must be concerned in the production of this radiation.

For the barium flame line $\lambda = 5535$, the limit could not be reached, as the interferometer used was not made to give differences of path greater than 240 mm., and at this difference of path the fringes were still very distinct. Even this incomplete result is sufficient to show that molecules are concerned in the production of the radiation.

The appearance of band spectra is usually associated with molecules, and the interpretation given to the results would require the recognition of the fact that molecules may give rise to line series as well as band spectra.

Another point arises. If two calcium or two strontium atoms can combine at the temperature of the electric arc, and yield spectrum lines peculiar to the compound, it might be possible for a calcium atom to combine with a strontium atom under the same conditions.

Experiments have been conducted to investigate this question. Photographs were taken in juxtaposition of the arc spectra of calcium, strontium, and a mixture of calcium and strontium, the apparatus used being a concave grating spectrograph giving a dispersion of 10 Å.U. per millimetre.

In the spectrum of the mixture no lines were found which did not occur in the spectra of either calcium or strontium. The matter, however, requires an explanation. Are calcium and strontium atoms, which are chemically very similar, able to combine to form Ca₂ and Sr₂, but yet unable to form the compound CaSr? Or does the calcium atom in CaSr yield the same spectrum as the calcium atom in Ca₂? It was hoped to investigate all the lines in the visible region of the calcium and strontium spectrum, but experimental difficulties have at present led to unsatisfactory With respect to the flame lines and the H and K lines, the arc will sometimes burn steadily for a considerable time, but the other lines in the spectrum flash in and out in a manner which makes measurement very In this respect the strontium spectrum was less troublesome than that of calcium. No exact results can be given for these lines, but it may be stated the limiting differences of path at which fringes were seen were generally less, and never greater, than would be expected on the assumption that the luminous particle was the atom, and no evidence has been found that particles of greater mass than the atom are concerned.

The Two Spectra of Argon.

The two spectra of argon appeared to be especially well suited to the study of the relative widths of arc and enhanced lines. At low pressures the red spectrum produced by means of an uncondensed discharge usually shows lines of the blue spectrum also, but under these conditions they are too faint for investigation with the interferometer, and a small condenser with a spark-gap in the circuit was necessary to develop the blue spectrum sufficiently brightly.

I am indebted to Prof. Herbert Jackson for the loan of two argon tubes of the ordinary Plücker form, but it was found necessary to make use of the greatly increased illumination obtainable with end-on tubes. The tubes were filled by admitting air, the diatomic constituents of which were removed, according to the well-known method of Prof. Soddy, by means of metallic calcium. Small pieces of calcium in a porcelain boat were heated in a quartz tube connected with the vacuum tubes, and air was admitted in small quantities until the tubes showed a pure argon spectrum.

As regards the red spectrum of argon, for $\lambda = 4511$, fringes were still just visible at 190 mm. difference of path, which gives N = 421,200, and putting M = 40, we get $T = 335^{\circ}$ Abs.

For the blue spectrum, excited by rather a weak condensed discharge, fringes were observed for the ray $\lambda = 4806$ up to a difference of path of 43 millimetres, which gives N = 89,471. Putting M = 40, we get $T = \text{about } 7400^{\circ} \text{ Abs.}$, an altogether inadmissible value.

It has been pointed out in a previous communication that the lines of the ordinary helium spectrum become wider when a condenser and spark-gap are introduced, keeping the current through the primary of the induction coil constant, and it was suggested that this broadening might be due to the sudden rise of temperature at each impulse. It is evident, however, that the differences in the widths of the lines in the red and blue spectra of argon are of a different order to any widening that can be accounted for in this manner.

The only other explanation at present provided for by theory is that the luminous particles concerned in the production of the blue spectrum are smaller than the particles from which the red spectrum originates. But this would lead to so low a value for the mass of the particle responsible for the blue spectrum that such an explanation could hardly be suggested in the absence of further evidence in this direction. It may be necessary to admit the existence of some hypothetical cause of broadening in this case, as Buisson and Fabry (loc. cit.) have done in the case of the Balmer series of hydrogen.

The Band Spectrum Associated with Helium.

The band spectrum associated with helium has been described by Goldstein* and by Curtis,† who has investigated the conditions most favourable to its production. More recently, Fowler‡ has made a more exhaustive investigation of this spectrum, and has made accurate measurements of the bands, resulting in the remarkable discovery of relations hitherto only associated with line spectra. Curtis (loc. cit.) found that the bands were best developed at moderately high pressures, and that with an uncondensed discharge they were faintly visible both in the capillary and in the bulbs, but that they could be obtained much more brightly by introducing a small capacity, with a short spark-gap in the circuit. Curtis points out that, although the spectrum in question is probably due to helium, this

^{* &#}x27;Deut. Phys. Ges.,' vol. 15, p. 10 (1913).

^{† &#}x27;Roy. Soc. Proc.,' A, vol. 69 (1913).

^{; &#}x27;Roy. Soc. Proc.,' A, vol. 91, p. 208 (1915).

cannot be regarded as definitely proven, owing to the presence of a trace of hydrogen in all his tubes.

Although little is known as to the origin of band spectra, it has usually been assumed that 2 atoms or more, at least indirectly, are concerned in their production, and the very existence of a band spectrum associated with helium must modify our outlook either on the origin of band spectra in general or on the usually accepted properties of helium.

For a number of vacuum tubes containing helium in a high state of purity I am indebted to Prof. Herbert Jackson, who has also given me his valuable help in some experiments on the effect of low temperatures on the band spectrum. The tubes were of the ordinary Plücker form, and showed no evidence of any impurity excepting a trace of hydrogen, which was just visible at the ends of the capillary,* and in one tube a trace of mercury, which disappeared after the tube had been run for a few minutes.

In the experiments at low temperatures, the tubes were excited by a moderately weak discharge from the induction coil, the intensity of the discharge corresponding to about one-third of an inch spark in air. No condenser or spark-gap was used, and the spectrum of the pink glow surrounding the electrodes was observed. The spectra were photographed with the single-prism spectrograph, and visual observations were also made.

In making the photographic observations, the glow from one of the electrodes was focussed on the slit of the spectroscope by means of a lens, and a definite exposure was given. The vacuum tube was then immersed in liquid air contained in an unsilvered vacuum vessel, and a second exposure was made for the same time, the second spectrum being photographed on the same plate in juxtaposition to the first. When the vacuum tube was wholly immersed in liquid air, the band spectrum appeared as before in both bulbs, but was much brighter than at room temperature. Photographs of the spectra of the tube at room temperature and at the temperature of liquid air show clearly the difference in the intensity of the bands. In the capillary, no change was observed.

The effect of immersing only the lower bulb of the tube in liquid air was very striking. The intensity of the band spectrum in the cooled bulb was greatly enhanced, the effect being especially noticeable in the case of the head at $\lambda = 6399$ Å.U. At the same time, the band spectrum entirely disappeared from the upper bulb, the upper electrode being surrounded by a green glow, showing the helium spectrum with the parhelium lines greatly enhanced.

When one bulb only is immersed, a lowering of the pressure would result, together with an increase of density in the cooled bulb. This would fall into

line with Curtis's observation (loc. cit.) that the band spectrum is more strongly developed at high pressures. It is evident that at ordinary temperatures the enhancement is due to the greater density at the higher pressure. When the discharge tube is totally immersed, there is clearly a lowering of the pressure without any appreciable change of density. Band spectra, in general, are known to occur more readily at lower temperatures, being usually ascribed to molecules, which at higher temperatures tend to dissociate into their constituent atoms. The enhancement of the band spectrum in helium at low temperatures, coupled with the very existence of a band spectrum associated with an inert gas, might justify the suspicion that in helium, though inert in the ordinary sense of the word, more than one atom may be involved in the processes resulting in the production of a band spectrum.

This suspicion is not confirmed by an investigation with the interferometer. For this purpose, it was found necessary to introduce a small capacity with a very small spark-gap into the circuit, since with the uncondensed discharge the spectrum is too feebly developed, and even with the condensed discharge the spectrum was too weak for visual observations. Photographs were taken in which the fringes for the lines of the band spectrum produced in this way were compared on the same plate with the lines of the ordinary helium spectrum produced with an uncondensed discharge. It was necessary in these experiments to employ a narrow slit in order to separate the components of the bands sufficiently for the fringes to be seen without confusion, and the lines of the bands in the neighbourhood of $\lambda = 4650$ could be successfully examined in this way. Only a very narrow strip of the ring system could, therefore, be examined, with the result that the limiting difference of path at which interference could be seen was considerably reduced, since the fringes are more difficult to distinguish in these very narrow strips.

The visibility of the fringes in this band spectrum and the ordinary lines appeared to be identical, and there was no evidence that the fringes for the band spectrum persisted at greater differences of path than for the ordinary lines. It can be seen that if the band spectrum were due to a helium molecule He₂ the ratio of the limiting differences of path would be about $\sqrt{2/1}$. It might be imagined that the lines of the band spectrum were broadened by the condensed discharge, in which case it would not be possible to conclude that any evidence against a molecular origin had been obtained. This is most unlikely. The condensed discharge employed was not powerful enough to broaden appreciably the ordinary helium lines. If the band spectrum of helium were analogous to the secondary spectrum of hydrogen,

or to part of it, as might reasonably be suspected, it would be concluded by analogy that the band spectrum would not be broadened by the condensed discharge, since Buisson and Fabry (loc. cit.) have shown that the lines of the secondary spectrum of hydrogen are not broadened under these conditions, whilst the reverse is the case with the Balmer series. It may, therefore, be considered extremely probable that the band spectrum is due to atomic belium.

The effect of low temperatures on the Balmer series and the secondary hydrogen spectrum has been investigated by Lemon,* who has found that at the temperature of liquid air the secondary spectrum is relatively This result may possibly be explained as being due to the condensation of minute traces of water vapour present on the walls of the tube at low temperatures, since it is well known that the presence of water vapour in hydrogen results in an enhancement of the lines of the Balmer series. A similar explanation may perhaps account for the enhancement of the band spectrum of helium at low temperatures, since this spectrum is adversely affected by the presence of impurities. The removal by condensation of impurities, which spectroscopically may not be detectable, might result in an enhancement of the band spectrum. It is probable that the trace of hydrogen which can be detected in almost every vacuum tube is present as water vapour; the hydrogen lines could not be detected at the temperature of liquid air in a neon tube in which they were brightly visible at ordinary temperatures.

The Characteristics of Series Lines.

From the characteristics of series of lines in spectra produced at atmospheric pressure, Rydberg, in his classical researches, was led to adopt the terms Diffuse and Sharp series. At the present time these terms do not denote the character of the lines in the series, but rather their numerical relations to one another and to the Principal series, and Kayser and Runge refer to these series as the First and Second subordinate series respectively, owing to the fact that the lines of the Diffuse series are not always diffuse in character. According to the circumstances which are at present recognised as determining the widths of spectrum lines, it might be supposed that the diffuse character of many Diffuse series lines at atmospheric pressure is due to the effect of collisions, which must be supposed to affect lines of the Diffuse series to a much greater extent than lines of the Sharp series.

^{* &#}x27;Astrophys. Journ.,' vol. 35, p. 109 (1912).

In the case of Diffuse and Sharp series, these characteristics of the lines disappear at low pressures, but re-appear when powerful condensed discharges are used to produce the radiations. It may be stated qualitatively that the lower the pressure the more powerful the discharge necessary to reproduce the characteristics of the lines. As a very striking instance of this, the spectrum of helium may be cited. At a pressure estimated at about one millimetre of mercury, no differences could be detected in the limiting orders of interference of the lines in the visible spectrum. This confirms the observations of Buisson and Fabry (loc. cit.), who have concluded that particles of the same mass are concerned in the production of all the series. When, however, the tube was excited by a powerful condensed discharge, the diffuse character of the Diffuse series at once appeared, more especially in the parhelium series, and could easily be recognised under the small dispersion of a single prism without the use of the interferometer. The experiment would appear to show that the difference in character between Diffuse and Sharp series is a general one under suitable conditions of electrical excitation, and would indicate that calculations of the actual mass of the luminous particles must be accepted with some reserve, especially in cases in which the law has not been experimentally verified under identical conditions of excitation. An inferior limit for the mass may be determined with confidence.

The Band Spectrum Associated with Helium.

By J. W. Nicholson, M.A., D.Sc., Professor of Mathematics in the University of London.

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A very significant addition to our knowledge of the nature of band spectra has been made by Prof. Fowler,* who has lately described the results of his examination of the band spectrum found in connection with helium and hydrogen, and believed to be a spectrum of helium. For Halm† has maintained that the formulæ which must be used to represent line and band spectra are intimately associated, and, in fact, spectroscopists have been generally inclined to suspect that the laws of line spectra have some counterpart in band spectra also. Fowler has taken the first step in the elucidation of this connection by showing that the universal constant of Rydberg belongs to this individual band spectrum, which contains two series of double "heads" arranged essentially in the same manner as the lines in a series spectrum.

One feature, however, of these double "heads" or doublets appears at first sight to differentiate them from the doublets found in line spectra, and one purpose of this paper is to show that the difference in character is only apparent, and that the formal analogy with line spectra extends very far. In ordinary Diffuse or Sharp series of doublets, the intervals between the components, when expressed in wave numbers, are constant, whereas in a Principal series the intervals rapidly become smaller, and vanish at the limit of the series. The intervals decrease, moreover, in a very regular manner. In the band-doublets discussed by Fowler, although the intervals decrease as the series proceed towards their limits, the decrease is not very regular, as shown by the differences, and the intervals do not obviously vanish at the limits. Without a very precise arrangement in series, it is not possible to judge of their limiting behaviour.

Fowler has shown that the less refrangible components can be arranged in series of a very ordinary simple form, that of Rydberg being almost sufficient. But the more refrangible components cannot be arranged in a satisfactory manner, even in a Hicks series. They are, in fact, an example of a phenomenon not unknown in line spectra, where lines which obviously belong to a series cannot be fitted in a satisfactory way into the usual formulæ, because those formulæ do not, in these individual cases, converge with sufficient rapidity.

^{* &#}x27;Roy. Soc. Proc.,' A, vol. 91, p. 208 (1915).

^{† &#}x27;Roy, Soc. Edin. Trans.,' vol. 41 (1906).

It will become apparent in the paper that this approximate superposition of two series with the same limit, but with very different modes of convergence among their coefficients, is the cause of the unusual character of the doublet separations. Fowler has already suggested that these two phenomena are related, but has not carried the calculations to the extreme point which can decide whether the separations are of a new type or not.

Two series of doublets have been noticed. In the first series, three have been measured with some accuracy, and six others in a more approximate manner. In the second series, there are four members, all well measured, and this series may be most conveniently discussed first. Its wave numbers, expressed in International units in vacuo, are

and the separations are respectively 95.7, 82.6, 72.2, 62.8. Fowler has represented the less refrangible components by the formula

$$\nu = 31956 \cdot 22 - 109679 \cdot 22/(m + 0.964402)^{2}, \tag{1}$$

which only gives errors 0.0, 0.7, 1.1, 0.0, and there is no doubt that these components follow the usual laws of series.

The simple Rydberg formula calculated for the other components is

$$\nu = 32014 \cdot 42 - N/(m + 0.968866)^{2}, \tag{2}$$

with errors 0.0, 9.4, 7.1, 0.0, and is not satisfactory. Fowler has, therefore, added one more constant, and, calculating from the first, second, and fourth lines, obtains

$$\nu = 32005.66 - n/(m + 0.982328 - 0.024835/m)^{3}, \tag{3}$$

with errors 0.0, 0.0, 2.9, 0.0. This is more satisfactory, but not completely so. The limiting doublet separations become, in the two cases, 58.2, 49.4, and we are led to the question of a possible further reduction of these separations by formulæ of increasing accuracy.

In order to test this point, we may notice that in a formula

$$\nu = A - N/D_{m^2}$$

where D_m proceeds in inverse powers by a series which is not very convergent, a more accurate limit will be obtained by calculations which do not include the first line, in which the divergence is most serious, provided, of course, that all the lines are measured with an equal degree of accuracy. This is the case for the four lines of the present series. Calculating, therefore, from the second, third, and fourth lines and using the better form of the series

$$D_m = m + \mu + \frac{\alpha}{m + \mu},\tag{4}$$

obtained in a preceding paper on the line spectrum of helium,* we can obtain the limit more accurately. Since μ is nearly unity,

$$D_m = m + \mu + \frac{\alpha}{m+1} \tag{5}$$

will serve almost equally well. Adopting this form, the calculated limit becomes

$$A = 31992.9. (6)$$

This already further reduces the limiting separations by 12.6, and it now becomes 36.7, representing the best value which can be obtained by a formula involving only three lines.

The next step in the demonstration makes use of all the four lines for the calculation of a formula with an extra constant, and of the more appropriate form. The final result of this calculation is

$$\nu = 31982 \cdot 8 - 109679 \cdot 2/D_m^2,$$
where
$$D_m = m + 1 \cdot 069416 - \frac{0.55971}{m + 1 \cdot 069416} + \frac{0.80624}{(m + 1 \cdot 069416)^2}.$$
 (7)

The limit falls 10 more units, the divergence of the doublets at the limit being now only about 27 units. This is not the most accurate formula which can be obtained from the four lines, and it is not yet very convergent for the earlier lines. It is evident that the next term in D_m will be important in the lines m=2,3, and, therefore, that the limit is still incorrect. Since every improvement in the formula has led to a marked depression in the limit, which now only differs by about 27 from the value for the companion series, there is every reason to believe that the limits are actually identical, and that the correspondence with line series extends further than the occurrence of the series relation.

The most accurate formula which can be obtained from the four lines is calculated as shown below, and involves a further decrease in the limit. Details of the calculation are given, as it takes the form which appears to be most convenient for general application. Writing the limit of the series as

$$A = 31955.9 + \delta A$$

where δA is small, and

$$\nu_m = A - N/\rho_m^2$$
 $(m = 2, 3, ...),$ (8)

31955.9 being a more exact limit for the other components with a simpler law, and N being the Rydberg constant, we find for the four lines, on calculation,

$$\rho_{2} = 2.975883 - 0.00012014 \,\delta A
\rho_{8} = 3.988380 - 0.00028922 \,\delta A
\rho_{4} = 5.005990 - 0.00057189 \,\delta A
\rho_{5} = 6.026428 - 0.00099775 \,\delta A$$
* 'Roy. Soc. Proc.,' A, vol. 91, p. 255 (1915).

If the four values are fitted into a formula,

$$\rho_{m} = m + \mu + \frac{\alpha}{m + \mu} + \frac{\beta}{(m + \mu)^{2}} + \frac{\gamma}{(m + \mu)^{3}},$$
 (10)

known already to be most appropriate to the helium line series, we easily obtain

$$(5+\mu)^3\rho_5 - 3(4+\mu)^3\rho_4 + 3(3+\mu)^3\rho_3 - (2+\mu)^3\rho_2 = 24\mu + 84,$$
 (11)

which is a cubic for μ . Neglecting the portions of the ρ 's dependent on δA , it becomes

$$-0.002285 \,\mu^3 + 0.011742 \,\mu^2 - 5.532276 \,\mu + 7.405136 = 0, \tag{12}$$

whence $\mu = 1.341395$. The correction to this value, dependent on δA , is, if $\delta \rho$ is the corresponding correction for any number ρ , determined by

$$3 \delta \mu \left\{ (5+\mu)^2 \rho_5 - 3 (4+\mu)^2 \rho_4 + (3+\mu)^2 \rho_3 - (2+\mu)^2 \rho_2 - 8 \right\}$$

= $- \left\{ (5+\mu)^3 \delta \rho_5 - 3 (4+\mu)^3 \delta \rho_4 + 3 (3+\mu)^8 \delta \rho_3 - (2+\mu)^3 \delta \rho_2 \right\},$

and ultimately

$$\mu = 1.341395 - 0.01152 \,\delta A. \tag{13}$$

With the extreme value of δA which is possible, we can show γ to be so small that for m=6, the term in γ does not contribute a significant amount to ρ_m , and the contribution to ρ_3 is small in comparison with that to ρ_2 . A similar calculation to the above, performed with m=3,4,5,6, would therefore give a result very close to that for m=3,4,5,6, only, and the value for (3,4,5) combined with that for (2,3,4,5) expressed in (13) will lead to a limit more accurate than even that in (7), although still not exact enough.

The calculation with m = 3, 4, 5, proceeds by writing

$$\rho_m = m + \mu + \frac{\alpha}{m+\mu} + \frac{\beta}{(m+\mu)^2},$$

whence

$$(5+\mu)^2\rho_5-2(4+\mu)^2\rho_4+(3+\mu)^2\rho_3=6\mu+24$$

and the ultimate solution by the preceding method is

$$\mu = 1.245914 - 0.006560 \,\delta A. \tag{14}$$

Combining the values (13) and (14) for the higher approximation available,

$$\delta A = 19.2, \quad \mu = 1.120211.$$
 (15)

The limit has again decreased by 8 units, and this decrease therefore continues to be systematic as formulæ of increasing accuracy, and of the type necessary in line spectra, are employed. The doublet separation is now only 18.9 at the limit as against the value 49.4 which accords with the best Hicks formula given by Fowler. It is evident, moreover, from a glance at the series below, and a comparison with (7), that it is not yet in any way

absolute, and that if even another line were available for calculation, the limit would again fall. This final series is

$$\nu_m = 31975 \cdot 1 - 109679 \cdot 2/\rho_m^2$$

where

$$\rho_m = m + 1.120211 - \frac{1.0211}{m + 1.120211} + \frac{2.2384}{(m + 1.120211)^2} - \frac{1.4974}{(m + 1.120211)^3}.$$
(16)

That δA is certainly much less even than 19.2 can be proved at once. For a calculation from the first three lines gives, by this method,

$$\mu = 1.160446 - 0.003384 \,\delta A. \tag{17}$$

This cannot be so accurate as (14), which again is not so accurate as (13).

Let us suppose that (13), which has the least error, and uses all four lines simultaneously, is correct. Then the errors in (17) and (14) are mainly derived from neglect of the term in γ , and are roughly in the ratio $(4+1)^3/(3+1)^3=2$. If, therefore, ϵ is the error in (14), we may write with a close approximation

$$\mu' = 1.341395 - 0.01152 \delta A
= 1.245914 - 0.006560 \delta A + \epsilon
= 1.160446 - 0.003384 \delta A + 2\epsilon$$
(18)

and, solving these three equations,

$$\delta A = 5.6$$

This is the most probable value of δA which can be derived from the four doublets, and it is very conclusive. We can now hardly doubt that the limit is identical with that of the simpler series. On this supposition, the doublet series is analogous to a Principal series in line spectra. Without measurements of further members of the more refrangible components, however, no formula can be given for these members of a much more satisfactory character than (7), and the question of the relation of the constants μ , α , ..., to those of known helium series cannot be investigated. The rapid change of these constants with the addition of an extra term to the formula precludes any precise specification of their values at present.

The First Series of Doublets.

The other series of doublets isolated by Fowler has for its leading members the wave numbers given in the Table, where δn denotes the doublet separations, and δn_1 , δn_2 , their first and second differences.

n .	m.	ðn.	δn_1 .	δn_2 .	n.	773.	δn.	δn_i .	δn ₃ .
21506 ·3 21613 ·7	2	107 -4	21 .0	11 5	32552 ·9 82591 ·6	7	38 .7	8.6	0.6
27192 ·1 2 7277 ·6	3	85.5	10 4	-8.2	82920 ·0 82956 ·9	8	36 -9	1 .8	6.8
29785 -2 29860 -8	4	75 ·1	18 6	9 ·4	83185 ·6 83210 ·9	9	25 -3	11.6	-9.8
31178 ·6 31235 ·1	5	56 .2	9 ·2		83379 ·0 83401 ·0	10	22 0	8.3	8.3
32014 ·4 32061 ·7	6	47 .3							

The differences appear to be quite irregular, although there is a remarkable oscillation in the second differences. A study of the values of δn indicates a definite convergence towards zero, but in an irregular manner. This irregularity is exactly of the type which would be expected if the more refrangible components followed a series law of the form

$$\nu = A - B/\rho_m^2,$$

where

$$\rho_m = m + \mu + \frac{\alpha}{m+\mu} + \frac{\beta}{(m+\mu)^2} + \dots,$$

the coefficients α , β , γ ,..., not converging rapidly to zero, and being alternately positive and negative, whereas in the corresponding series for the less refrangible components, the convergence of α , β , γ , to zero is rapid. The preliminary series given by Fowler accord with this result. For the less refrangible components, he finds a simple Rydberg formula,

$$\nu = 34295.86 - 109679.22/(m + 0.928427)^{2}, \tag{20}$$

to be nearly satisfactory, and a corresponding Hicks formula does not show much improvement. It must be borne in mind, of course, that only the first three doublets are measured with great accuracy, although the next three or four must be fairly accurate. The later values are admittedly approximate.

A formula of the proper generalised Rydberg type has been calculated from the first four lines of this simple series, and the result is

$$\rho_m = m + 0.907876 + \frac{0.34020}{m + 0.907876} - \frac{1.54661}{(m + 0.907876)^2} + \frac{2.12558}{(m + 0.907876)^3}.$$
(21)

The limit is almost exactly that obtained by Fowler from the simpler series, VOL. XCI.—A. 2 M

which he concluded must be nearly correct. But the discrepancies between observed and calculated values given by the simpler formula cannot be removed without using a formula with comparatively large values of α , β , and γ . The difference between the two types of series into which the more and the less refrangible components fall is, therefore, not so pronounced as appears at first sight.

The problem of determining the limit of the more refrangible associated series remains.

The application of the simple Rydberg and the Hicks formulæ by Fowler gives for this series the limits 34330·18, 34324·72, the more accurate formula giving a limit nearer to that of the less refrangible series of components. Fowler has also used a Hicks formula with an extra constant, giving a limit 34310·97, which is again noticeably nearer. But even this formula is by no means satisfactory as a representation of the lines, and the steady decrease which has already taken place in the limit with each improvement in the representation, combined with the results of our examination of the other set of doublets, leaves little doubt that this series of doublets is also of a Principal type, if the calculation is pushed further. For even the apparent limiting separation of the doublets is by no means so large as it was in the first series with which this paper deals. The complete investigation follows so closely along the lines already described for the other doublet series that there is no need to give it in detail here. One or two of its main features may be mentioned.

If the limit of the series is taken as $34296.1 + \delta A$, the values of ρ_m in

$$\nu = A - B/\rho_{m}^{2}$$

$$\rho_{2} = 2.940786 - 0.00011595 \delta A$$

$$\rho_{3} = 3.953183 - 0.00028168 \delta A$$

$$\rho_{4} = 4.972534 - 0.00056069 \delta A$$

$$\rho_{5} = 5.985934 - 0.00097825 \delta A$$

$$\rho_{6} = 7.006214 - 0.00156886 \delta A$$

$$\rho_{7} = 8.021678 - 0.00235516 \delta A$$

$$\rho_{8} = 9.049840 - 0.00338261 \delta A$$

$$\rho_{9} = 10.053262 - 0.00463841 \delta A$$

The last figures are not very reliable beyond ρ_4 , and even the last three figures may be incorrect in later entries.

Fowler's Hicks formula was derived from the first, second and seventh times. The seventh may not be very accurate, and the first should not be used in the problem of merely determining the limit accurately, which is our present purpose.

are

Applying the Hicks formula to the second, third and fourth lines, as the most suitable and accurate trio, in the form

$$\rho_m = m + \mu + \frac{\alpha}{m} \qquad (m = 2, 3, 4),$$

we find

$$\delta A = 5.54.$$

But on the theory of the preceding paper, a better value must be given by

$$\rho_m = m + \mu + \frac{\alpha}{m + \mu} = m + \mu + \frac{\alpha}{m + 1}$$

nearly, for μ is evidently close to unity. This leads to $\delta A=2\cdot 16$ or very nearly zero. On the supposition, therefore, that the second, third and fourth lines are measured accurately, the limit of the series is almost certainly that of the less refrangible components. Further examination on these lines need not be given, but we may perhaps notice that with $\delta A=0$ we can deduce a formula with three constants

$$\nu = 34296 \cdot 1 - 109679 \cdot 22/\rho_m^2,$$

$$\rho_m = m + 1 \cdot 16802 - \frac{1 \cdot 30932}{m + 1 \cdot 16802} + \frac{1 \cdot 99441}{(m + 1 \cdot 16802)^2},$$

from the first three lines, which is as satisfactory as that calculated by Fowler according to the Hicks model and with a later line. With the same number of constants, more satisfactory formulæ have been obtained throughout when the generalised Rydberg form has been used.

Summary.

- 1. The paper gives further support to Fowler's conclusion that the heads of the bands in the band spectrum of Goldstein and Curtis follow ordinary line-series laws, by showing that the doublet separations tend to zero at the limits of the series.
- 2. Both the doublet series isolated by Fowler are strictly analogous to Principal series in line spectra.
- 3. The generalised Rydberg formula gives the most suitable representation of these series as well as of line series.

On the Shapes of the Equipotential Surfaces in the Air near Long Walls or Buildings and on their Effect on the Measurement of Atmospheric Potential Gradients.

By CHARLES H. LEES, D.Sc., F.R.S.

(Received May 10, 1915.)

§ 1. In considering the most suitable arrangements for recording the variations of the atmospheric potential gradient at the East London College, where no large horizontal surface is available, I have had occasion to calculate the distribution of potential in the neighbourhood of walls and buildings of simple shapes. As the results can be applied in practice it seems advisable to put them on record for the use of other observers.

Observation shows that during fine weather the potential at a point in the atmosphere over a level portion of the earth's surface in these latitudes increases as the point is raised, at the rate of about 150 volts per metre. This rate of increase diminishes slowly as the point ascends, owing to the slight excess of positive over negative ions in the air near the earth's surface, and at an altitude of a kilometre is reduced to about 25 per cent. of its value at the surface.*

The potential differences between points on the earth's surface 1000 metres apart or between a point on the surface of a building and one on the ground near it are found to be small compared to those present in the atmosphere.

For the present purpose we shall neglect the small effect of the ions near the earth's surface on the potential gradient for the first few metres above the surface and shall treat the earth's surface as plane and the earth and buildings as being conductors.† In order further to simplify the problem as much as possible, the walls of the buildings are taken to be long in comparison to their heights, so that the effects of the corners on the distribution of

^{*} The article "Atmospheric Electricity," by Chree, in the 'Encyclopædia Britannica,' 11th edition, or that by Gerdien in the 'Handbuch der Physik,' vol. 4, p. 687, or Mache and von Schweidler's 'Atmospherische Elektrizität,' chap. I, may be consulted for accounts of the methods used and the results obtained. For recent results obtained at Kew, Chree ('Phil. Trans.,' A, vol. 206, p. 299 (1906), and A, vol. 215, p. 133 (1915)) and Dobson ('Proc. Phys. Soc. Lon.,' vol. 26, p. 334 (1914)) may be consulted.

⁺ Benndorf ('Wiener Ber.,' vol. 109, p. 923 (1900), vol. 115, p. 425 (1906)) has determined with the same simplifications the changes in the vertical potential gradients near a long plateau with rounded edges, a circular plateau, and an ellipsoidal column. Sir J. Larmor and J. S. B. Larmor ('Roy. Soc. Proc.,' A, vol. 90, p. 312 (1914)) give diagrams of potential surfaces, etc., for an ellipsoidal column and an earth-connected sphere.

potential near the middle of their length may be neglected. The walls are further taken to be vertical, and in the case of more than one to be parallel to each other. Roofs are taken to be horizontal.

§ 2. Case I.—A long thin vertical wall projects from a horizontal surface above which, at a considerable distance from the wall, the potential gradient is constant. To find the distribution of potential near the wall.

Take the z plane, where z = x + iy, vertical and perpendicular to the wall, the x axis along the horizontal plane, and the y axis up the wall. If h is the height of the wall, the Schwarzian transformation $dz/dw = hw(w^2 - \alpha^2)^{-1}/\alpha$, where w = u + iv, converts the x and y axes into the axis of u in the w plane and the first quadrant in the former into the first two quadrants in the latter plane. Integrating, we have

$$z/h = (w^2/\alpha^2 - 1)^{\frac{1}{2}}$$
 or $w^2/\alpha^2 = z^2/h^2 + 1$. (1)

If P is a point in the air whose bi-polar co-ordinates are $r\theta$, $r'\theta'$, from the top of the wall and from the image of the top in the plane respectively, the last equation gives us at P

$$u = \sqrt{(rr')} \cdot \cos \frac{1}{2} (\theta + \theta'), \qquad v = \sqrt{(rr')} \cdot \sin \frac{1}{2} (\theta + \theta'). \tag{2}$$

Thus the potential v at any point whose bi-polar co-ordinates are given is easily calculated.

To calculate the potential at a point whose co-ordinates are x, y, or to draw the surfaces of equal potential, it is more convenient to use equation (1), which gives on equating separately the real and unreal parts

$$(u^2-v^2)/\alpha^2 = (x^2-y^2+h^2)/h^2$$
 $uv/\alpha^2 = xy/h^2$,

and on eliminating u,

$$(\alpha^2/h^4)(x^2y^2/v^2) - v^2/\alpha^2 = (x^2 - y^2 + h^2)/h^2.$$

Thus the potential at the point x, y, is given by

$$v^{2} = (\alpha^{2}/2h^{2}) \left\{ \sqrt{\left[(x^{2} - y^{2} + h^{2})^{2} + 4x^{2}y^{2} \right] - (x^{2} - y^{2} + h^{2})} \right\}$$
(3)

and the factor by which the observed potential v at the point x, y, should be multiplied to give the potential at the height y above an infinite plane is

$$\frac{y}{(\alpha/\sqrt{2\,h})\,\sqrt{\,\{\sqrt{\,[(x^2\!-\!y^2\!+\!h^2)^2\!+\!4\,x^2y^2]\!-\!(x^2\!-\!y^2\!+\!h^2)\}}}\,.$$

The equipotential lines are readily drawn from the equation

$$y^2 = \frac{h^2 + x^2 + h^2 v^2 / \alpha^2}{1 + \alpha^2 x^2 / h^2 v^2}.$$
 (4)

They are shown in fig. 1* for the case h = 1, $\alpha = 1$.

* I have to thank Lieut. B. Barnes, 10th East Surreys, one of my senior students, for drawing these curves.

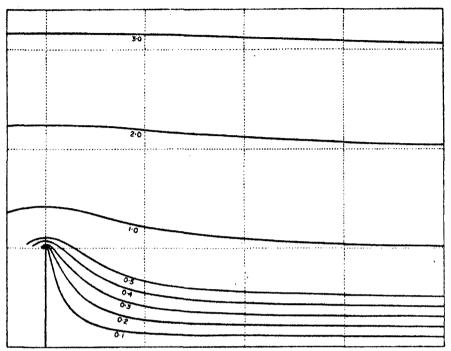


Fig 1.—Section of the equipotential surfaces near the middle of a long thin wall.

§ 3. If x is constant we have, since $w = (\alpha/h)\sqrt{(z^2 + h^2)}$,

$$\Big(\frac{\partial u}{\partial y}\Big)_x + i\Big(\frac{\partial v}{\partial y}\Big)_x = \frac{\alpha}{h} \frac{-y + ix}{\sqrt{(x^2 - y^2 + h^2 + 2ixy)}}.$$

If, further, y = 0, then

$$\left(\frac{\partial u}{\partial y}\right)_x = 0$$
 and $\left(\frac{\partial v}{\partial y}\right)_x = \frac{\alpha}{h} \frac{x}{\sqrt{(x^2 + h^2)}} = \frac{\alpha}{h}$ (5)

when x is infinitely large.

The last two equations show that the ratio of the vertical potential gradient at a point on the ground to the normal vertical gradient is equal to the cosine of the angle subtended at the point by the height of the wall.

The following Table* shows the vertical gradient at points on the ground whose distances from the foot of the wall are given in terms of the height of the wall.

^{*} This Table and the corresponding ones on pp. 445 and 449 are added at the suggestion of Dr. Chree so as to be available for discussion of the effects of vertical potential gradients on plants and animals.

Distance from foot Height	Vertical gradient Normal	Distance from foot Height	Vertical gradient Normal	
0.0	0.0	1 '5	0 .832	
0.2	0 ·196	2.0	0.894	
0.4	0.371	3.0	0.949	
0.6	0.515	4 .0	0.970	
0 ·8	0.625	5.0	0.981	
1.0	0.707	10.0	0.995	

Table of Ratios of Vertical Gradient to the Normal Vertical Gradient at-Points on the Ground near the Middle of a Long Thin Vertical Wall.

§ 4. If y is constant we have in the same way

$$\left(\frac{\partial u}{\partial x}\right)_{y}+i\left(\frac{\partial v}{\partial x}\right)_{y}=\frac{\alpha}{h}\frac{x+iy}{\sqrt{(x^{2}-y^{2}+h^{2}+2ixy)}}.$$

At x = 0 this gives, if y is less than h,

$$\left(\frac{\partial u}{\partial x}\right)_{y} = 0, \ \left(\frac{\partial v}{\partial x}\right)_{y} = \frac{\alpha}{h} \frac{y}{\sqrt{(h^{2} - y^{2})}}.$$
 (6)

The horizontal potential gradient at y' on the wall is therefore identical with the normal vertical gradient if

$$y'^2 = h^2 - y'^2,$$

 $y' = h/\sqrt{2} = 0.707h.$

that is if

As we proceed outwards from the wall the horizontal potential gradient decreases, but at the height 0.707h we may move outwards a distance 0.1h without the potential being 1 per cent. less than that which would have been found at the point if the horizontal gradient had remained constant and equal to the normal vertical gradient. At a distance 0.25h from the wall the potential is 5 per cent. less than the normal gradient would give.

At larger distances from the wall the change of potential should be calculated directly from either of the expressions (2) and (3) for it in terms of the co-ordinates of the point.

§ 5. Case II.—A long vertical retaining wall separates from each other two horizontal plane surfaces over which the potential gradient at a considerable distance from the wall is the same and independent of height above the planes. To determine the distribution of potential near the wall.

Taking the z plane, where z = x + iy, vertical and perpendicular to the retaining wall, the x axis along the lower plane, and the y axis up the surface of the wall, we have the Schwarzian transformation

$$dz/dw = a\sqrt{\{(w+\alpha)/(w-\alpha)\}/\alpha},$$

and

which converts the lower boundary of the atmosphere in the z plane into the axis of u in the w plane, where w = u + iv.

Writing $w/\alpha = \cosh \zeta$, the equation becomes $z = a \int (\cosh \zeta + 1) d\zeta$, the integral of which is

$$z = a \left(\sinh \zeta + \zeta \right). \tag{7}$$

Expanding and separating real and unreal parts, we have

$$u/\alpha = \cosh \xi \cos \eta, \qquad v/\alpha = \sinh \xi \sin \eta w/\alpha = \sinh \xi \cos \eta + \xi, \qquad y/\alpha = \cosh \xi \sin \eta + \eta$$
 (8)

If v = 0 we must have either $\xi = 0$ or $\eta = 0$ or π .

In the first case x = 0, in the second y = 0, in the last $y/a = \pi$. The height h of the wall is therefore equal to $a\pi$, that is $a = h/\pi$, and the equations connecting w and z may be written

$$w/\alpha = \cosh \zeta, \quad \pi z/h = \sinh \zeta + \zeta.$$
 (9)

To find the potential v at a given point x, y, it is necessary to solve for ξ , η , the second set of transcendental equations (8) or (9), and substitute the values of ξ and η in the equation for v.

To draw the equipotential surfaces we use the equations:-

$$\frac{\pi(x/h) = (v/\alpha)\cot\eta + \operatorname{argsinh}(v/\alpha\sin\eta)}{\pi(y/h) = \sqrt{[(v^2/\alpha^2) + \sin^2\eta] + \eta}},$$
(10)

and assign to η all values from 0 to π and to v values exceeding 0.

The curves obtained are shown in fig. 2 for the case in which the height of the equipotential surface of potential unity is equal to that of the wall, that is $\alpha = 1/\pi$, and h = 1.

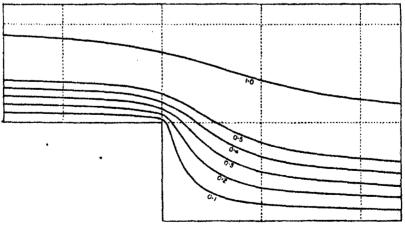


Fig. 2.—Section of the equipotential surfaces near the middle of a long retaining wall.

On differentiating equations (9) we have

$$(1/\alpha)du = \sinh \xi \cos \eta \, d\xi - \cosh \xi \sin \eta \, d\eta$$

$$(1/\alpha)dv = \cosh \xi \sin \eta \, d\xi + \sinh \xi \cos \eta \, d\eta$$

$$(\pi/h)dx = \cosh \xi \cos \eta \, d\xi - \sinh \xi \sin \eta \, d\eta + d\xi$$

$$(\pi/h)dy = \sinh \xi \sin \eta \, d\xi + \cosh \xi \cos \eta \, d\eta + d\eta$$
(11)

§ 6. If w is constant we have

$$\cosh \xi \cos \eta \, d\xi - \sinh \xi \sin \eta \, d\eta + d\xi = 0.$$

Thus

$$(1/\alpha)dv = \left(\frac{\cosh \xi \sinh \xi \sin^2 \eta}{\cosh \xi \cos \eta + 1} + \sinh \xi \cos \eta\right)d\eta,$$

and

$$(\pi/h) dy = \left(\frac{\sinh^2 \xi \sin^2 \eta}{\cosh \xi \cos \eta + 1} + \cosh \xi \cos \eta + 1\right) d\eta.$$

Hence the vertical potential gradient at the point corresponding to ξ , η , is given by

$$\left(\frac{\partial v}{\partial y}\right)_{x} = \frac{\alpha \pi}{h} \frac{\sinh \xi}{\cosh \xi + \cos \eta}$$

$$= \frac{\alpha \pi}{h} \frac{\sinh \xi}{\cosh \xi + 1} \quad \text{if } \eta = 0,$$

$$= \frac{\alpha \pi}{h} \frac{\sinh \xi}{\cosh \xi - 1} \quad \text{if } \eta = \pi.$$
(12)

In each case $\left(\frac{\partial v}{\partial y}\right)_z = \frac{\alpha \pi}{h}$ if ξ is large.

The vertical potential gradient is therefore $\alpha\pi/\hbar$ over both planes at considerable distances from the retaining wall. At smaller distances it is less than the normal over the lower and greater than it over the upper plane.

Table of Vertical Gradient Normal Vertical Gradient, near the Middle of a Long Retaining
Wall or Flat-roofed Building.

Lower surface.		Upper surface.	
Distance from foot Height	Gradient Normal	Distance from top Height	Gradient Normal
0.0	0.0	0.0	9 0
0 ·127	0.100	0.056	2 16
0.258	0 ·198	0.200	1 .28
0.388	0 .292	0.218	1 .81
0 .587	0.880	2 ·23	1 '11
0.690	0 .462	22.0	1 '01
1 ·154	0.686		
1 .79	0 .761		
4.13	0.909	1	
25 .2	0.987		

The preceding Table gives in terms of the normal gradient the vertical gradient at points whose distances from the foot and top of the retaining wall on each of the horizontal surfaces are expressed in terms of the height of the wall.

§ 7. If y is constant we have

$$\sinh \xi \sin \eta \, d\xi + (\cosh \xi \cos \eta + 1) \, d\eta = 0.$$

Thus
$$(1/\alpha) dv = \left(\cosh \xi \sin \eta - \frac{\sinh^2 \xi \cos \eta \sin \eta}{\cosh \xi \cos \eta + 1}\right) d\xi,$$
 and
$$(\pi/h) dx = \left(\cosh \xi \cos \eta + 1 + \frac{\sinh^2 \xi \sin^2 \eta}{\cosh \xi \cos \eta + 1}\right) d\xi.$$

Hence the horizontal potential gradient at the point corresponding to ξ , η , is given by

$$\left(\frac{\partial v}{\partial x}\right)_{y} = \frac{\alpha \pi}{h} \frac{\sin \eta}{\cosh \xi + \cos \eta}$$

$$= \frac{\alpha \pi}{h} \frac{\sin \eta}{1 + \cos \eta}; \quad \text{if } \xi = 0, \text{ that is when } x = 0. \tag{13}$$

It will be noticed that the ratio of the vertical to the horizontal gradient at the point corresponding to ξ , η , is $\sinh \xi / \sin \eta$.

The horizontal potential gradient close to the wall will be identical with the vertical gradient over the planes at great distances from the wall if

$$\sin \eta = \cos \eta + 1,$$
$$\eta = \pi/2.$$

that is if

The point y' on the wall corresponding to $\xi = 0$, $\eta = \pi/2$, is given by

$$u' = h(\sin n + n)/\pi = h(1 + \pi/2)/\pi$$

Hence the point on the wall at which the horizontal gradient outwards is equal to the normal vertical gradient is at a height equal to $(1+\pi/2)/\pi$ of the total height of the wall, that is to 0.818 of the total height.

As we proceed outwards from the wall at this height the horizontal potential gradient decreases, but at a distance from the wall not exceeding 0.1 of the height of the wall the potential is less than 2 per cent. smaller than it would be if the horizontal gradient had been equal to the normal vertical gradient for the whole distance.

§ 8. Case III.—Two long thin vertical walls parallel to each other rise to the same height above a horizontal plane. To find the distribution of potential in the space between the walls.

To simplify the calculation we shall take the walls as being two consecutive walls of a regular series extending on both sides to infinity. Taking the x plane, where z = x + iy, vertical and perpendicular to the series of planes, the x axis along the horizontal plane, and the y axis vertical through the point on the x axis half way between the planes, the transformation $\sin w = \alpha \sin(z/a)$, where α and α are constants, α being less than unity, converts the lower boundary of the atmosphere into the axis of u in the w plane, where w = u + iv.

Expanding the circular functions we have

$$\sin u \cosh v = \alpha \sin (x/a) \cosh (y/a)
\cos u \sinh v = \alpha \cos (x/a) \sinh (y/a)$$
(14)

and

If v = 0, $\cos(x/a)\sinh(y/a) = 0$, and $\sin u = \alpha \{\sin(x/a)\cosh(y/a)\}$. Thus either y = 0 or $(x/a) = \pm (2n+1)\pi/2$, where n is an integer.

If y = 0, $\sin u = \alpha \sin (x/a)$, and u and x increase from zero together till $x = a\pi/2$ and $u = \arcsin \alpha$.

If $x/a = \pi/2$, $\sin u = \alpha \cosh(y/a)$, and y increases from zero to a argcosh $1/\alpha$, while u increases from $\arcsin \alpha$ to $\pi/2$.

The distance δ of the walls apart is therefore $= a\pi$, and their height h is $a \operatorname{argcosh}(1/\alpha)$. Hence $a = \delta/\pi$, $\alpha = 1/\cosh(\pi h/\delta)$, and the equation connecting w and z may be written

$$\sin w = \sin(\pi z/\delta)/\cosh(\pi h/\delta). \tag{15}$$

The equation to the equipotential lines is therefore

$$\frac{\sin^2(\pi x/\delta)\cosh^2(\pi y/\delta)}{\cosh^2 v} + \frac{\cos^2(\pi x/\delta)\sinh^2(\pi y/\delta)}{\sinh^2 v} = \cosh^2(\pi h/\delta), \quad (16)$$

a quadratic in $\sinh^2 v$ and $\cosh^2 v$ from which v at any point x, y, may be calculated and the reducing factor to convert readings taken at x, y, into readings in the open may be found.

In drawing the equipotential curves it is best to use the equation in the form

$$\cosh \frac{\pi y}{\delta} = \cosh v \sqrt{\left(1 + \frac{\sinh^2(\pi h/\delta)}{1 + \cos^2(\pi x/\delta)/\sinh^2 v}\right)}.$$

^{*} The somewhat more general transformation $\sin (w/\beta) = a \sin (z/a)$ may be treated in the same way throughout.

The equipotential curves are shown in fig. 3 for the case $\delta = \pi h$.

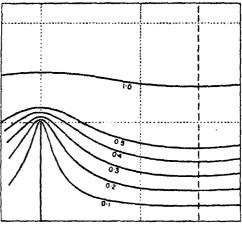


Fig. 3.—Section of the equipotential surfaces near the middle of one of a series of thin parallel walls. The thick dotted vertical line is midway between two planes.

§ 9. If x is constant we have, from equation (15)

$$\left(\frac{\partial u}{\partial y}\right)_x + i\left(\frac{\partial v}{\partial y}\right)_x = i\frac{\pi}{\delta} \frac{\cos\left[\pi\left(x+iy\right)/\delta\right]}{\sqrt{\left\{\cosh^3\left(\pi h/\delta\right) - \sin^3\left[\pi\left(x+iy\right)/\delta\right]\right\}}}.$$

At x = 0 this reduces to

$$\left(\frac{\partial u}{\partial y}\right)_x = 0$$
, and $\left(\frac{\partial v}{\partial y}\right)_x = \frac{\pi}{\delta} \frac{\cosh\left(\pi y/\delta\right)}{\sqrt{\left[\cosh^2\left(\pi h/\delta\right) + \sinh^2\left(\pi y/\delta\right)\right]}}$.

For large values of y this gives the normal vertical potential gradient = π/δ . At y = 0 it gives

$$\left\langle \frac{\partial v}{\partial y} \right\rangle_{z} = \frac{\pi}{\delta} \frac{\cos(\pi x/\delta)}{\sqrt{\left[\cosh^{2}(\pi h/\delta) - \sin^{2}(\pi x/\delta)\right]}},$$

$$\left(\frac{\partial v}{\partial y}\right)_{z} = \frac{\pi}{\delta} \frac{1}{\sqrt{\left[\sinh^{2}(\pi h/\delta) / \cos^{2}(\pi x/\delta) + 1\right]}}.$$
(17)

that is

At the point on the ground half-way between the planes

$$\left(\frac{\partial v}{\partial y}\right)_x = \frac{\pi}{\delta} \frac{1}{\cosh\left(\pi h/\delta\right)}.$$
 (18)

Thus the ratio of the vertical gradient on the ground half-way between the planes to the normal vertical gradient is $1/\cosh(\pi h/\delta)$.

The following Table gives the values of this ratio for different values of the ratio of height of planes to distance apart.

Table of Vertical Gradient on the Ground Midway between Two Vertical Planes for Different Ratios of Height of Planes to Distance apart.

Height Distance spart	Vertical gradient.	Height Distance apart	Vertical gradient.	Height Distance apart	Vertical gradient.
0.0	1.0	0.382	0.552	1 .273	0.0860
0.064	0.980	0.572	0.822	1 .592	0.0135
0 .127	0.925	0.768	0.180	1 910	0.0050
0.191	0 .844	0.954	0.099	,	

The vertical gradient at other points on the ground between the planes is given by the equation (17) above, and is tabulated below for several values of the ratio of height of the planes to distance apart.

Table of Vertical Potential Gradient on the Ground between Two Vertical Planes

Distance of point Distance of planes spart		Height of planes Distance apart		against a said,		
From plane.	From middle.	0 .064.	0 ·191.	0 ·382.	0 .763.	
0.0	0.2	0.0	0.0	0.0	0.0	
0.1	0.4	0 .844	0 445	0.201	0.056	
0 .2	6.0	0.946	0.679	0.865	0.107	
8.0	0.2	0 970	0 .783	0 .473	0.146	
0.4	0.1	0 .978	0.881	0 .233	0 .172	
0.2	0.0	0 .580	0 .844	0.552	0.180	

These figures are sufficient to show how great is the effect of the walls on the vertical gradient on the ground between them. They may be taken as representing with a fair degree of accuracy the vertical gradient on the ground in a street with buildings on each side of it.

§ 10. If y is constant we have

$$\left(\frac{\partial u}{\partial x}\right)_{y} + i\left(\frac{\partial v}{\partial x}\right)_{y} = \frac{\pi}{\delta} \frac{\cos\left[\pi (x+iy)/\delta\right]}{\sqrt{\left\{\cosh^{2}(\pi h/\delta) - \sin^{2}\left[\pi (x+iy)/\delta\right]\right\}}}.$$

At $x = \delta/2$ this becomes

$$\left(\frac{\partial u}{\partial w}\right)_{y} + i\left(\frac{\partial v}{\partial x}\right)_{y} = \frac{\pi}{\delta} \frac{-i\sinh\left(\pi y/\delta\right)}{\sqrt{\left\{\cosh^{2}\left(\pi h/\delta\right) - \cosh^{2}\left(\pi y/\delta\right)\right\}}}.$$

that is

If y is less than h, this gives

$$\left(\frac{\partial u}{\partial x}\right)_{y} = 0$$
, and $\left(\frac{\partial v}{\partial x}\right)_{y} = -\frac{\pi}{\delta} \frac{\sinh(\pi y/\delta)}{\sqrt{\left\{\cosh^{2}(\pi h/\delta) - \cosh^{2}(\pi y/\delta)\right\}}}$. (19)

If the horizontal potential gradient at y' on the wall is to be equal to the normal vertical gradient π/δ , we must have

$$\sinh^{2}(\pi y'/\delta) = \cosh^{2}(\pi h/\delta) - \cosh^{2}(\pi y'/\delta),$$

$$\sinh(\pi y'/\delta) = (1/\sqrt{2}) \sinh(\pi h/\delta).$$

When the height h becomes small compared to the distance apart δ of the planes, this gives the distance y' up the plane as 0.71 times the height, as was found by direct calculation.

The following Table gives the relation between the ratio of the height of the planes to their distance apart and the fraction of the height at which the horizontal potential gradient outwards is equal to the normal vertical potential gradient over a plane surface.

Height Distance apart	Fraction of height.	Height Distance apart	Fraction of height.
0.0	0.707	0 .445	0 · 790
0 .084	0.708	o · 5 09	0.807
0 .127	0.717	0.572	0.822
0 -191	0 .727	O -686	0 .836
0 .254	0.741		
0.818	0 .757	0 -795	0 .864
0 .382	0.778	0 .954	0 .886

As the planes approach each other the potential surfaces near their summits become more nearly horizontal, so that the potential gradient is more nearly vertical than horizontal.

§ 11. It follows from the previous work that where plane horizontal surfaces of considerable extent are not available for the determination of the normal vertical potential gradient in the atmosphere, observations in the neighbourhood of buildings can be utilised, the value of the reducing factor being calculated from the forms of the buildings in the simple cases dealt with. In many cases observations of the horizontal potential gradient outwards from the walls of buildings which are not too close together may be made, and, if the position of the point of observation is properly chosen, the horizontal gradient observed will be identical with the normal vertical gradient over a horizontal surface. For a long wall of a building with a flat roof or with a parapet, the horizontal gradient outwards should be measured

at a point near the middle of the length of the wall and at a distance up it which is generally about three-quarters of the height. The horizontal gradient for a distance outwards not exceeding 1/10 the height of the wall will not differ by more than 2 per cent. from the normal vertical gradient over a large horizontal area.

On the Enhanced Series of Lines in Spectra of the Alkaline Earths.

By W. M. Hicks, Sc.D., F.R.S.

(Received May 15, 1915.)

The problem of the limits and numerical relations between the lines of the enhanced series of doublets in the alkaline earths has for long been a difficulty to spectroscopists. Ritz* in 1908 gave arrangements for the Sharp series from Mg to Ra inclusive, and proposed series formulæ for Ca, Sr, Ba, in which alone he had three lines from which to calculate the constants. The absence of extra lines rendered it impossible to test his formulae, but the values of the constants obtained for his formulæ were quite out of line with those of the analogous constants in other series, and produced an instinctive doubt as to whether it gave the correct relation. It is now possible to test his limits by considering whether the denominator differences which give the observed separations have any relation to the oun or not. The result of this consideration is definitely adverse. In none of the three is it possible to make the differences multiples of the oun without supposing observation errors in the doublet separations which are quite inadmissible; and even then in the cases of Ca and Ba by taking odd multiples of δ_1 , which is never the case for S doublets in any other known series.

There can be little doubt but that Fowler† has at last settled this question by taking the Rydberg numerator constant to be 4N in place of N, thus combining in one set lines which on the old supposition would be arranged in two series, depending on Sharp and Principal sequences. The object of the present note is the determination of the connection of these series with certain laws which have been arrived at in previous communications; to this Society

^{* &#}x27;Phys. Zeitschr.,' vol. 16, p. 521.

^{† &#}x27;Phil. Trans.,' A, vol. 214, p. 225 (1914).

^{† &#}x27;Phil. Trans.,' A, vol. 210, p. 57 (1909); A, vol. 212, p. 33 (1912); A, vol. 213, p. 323 (1913)—referred to in the following as (I), (II), and (III) respectively.

and more especially their dependence on the quantity in (III) called the "oun." This is a quantity peculiar to each element, of magnitude $\delta_1 = 90.472w^2$, where w is 1/100 of the atomic weight. It is convenient to use $\delta = 4\delta_1$ in general. Their values as determined by observation are given in (III, pp. 344-346). The most doubtful is correct to at least 1 in 1000.

Fowler gives formulae for the elements Ca and Sr with the limits for the S, D, and F series and for the S, D series of Mg. These values will be used in what follows. In order to get a conspectus for the whole group I have added a discussion for the corresponding lines in Ba and Ra.

A few preliminary remarks on the series formula may not be out of place. In (II, p. 35) I have given reasons that in the triplet series of this group the S series depend on the sequence which in the alkalies give the P_1 , and vice versa. If we assume the same result for the doublet series it will be found that the new formulæ reproduce the other lines with much greater closeness than those used by Fowler—who has very naturally taken a Sharp sequence for a Sharp series. The modification consists in taking the constant μ as 1+fraction or, which comes to the same thing, writing the denominator as $m+\mu+\alpha/(m-1)$. The formulæ on this basis, using the first three lines for data, are

Ca.....
$$n = 70310 \cdot 5 - 4 \text{ N}/(m + 1 \cdot 205860 - 0 \cdot 065296/m)^2$$

Sr..... $n = 64466 \cdot 0 - 4 \text{ N}/(m + 1 \cdot 301682 - 0 \cdot 081502/m)^2$,

and the values of O-C, compared with Fowler's, are

In the case of Ba (as allocated below) the formulæ calculated from the second, third, and fourth reproduce the first line with values of O-C=-143 when $\mu=$ fraction, and 159 when $\mu=1+$ fraction. It is probable that a formula with $m+1+f+\alpha/(m+f)$ would reproduce the lines of each element with very fair accuracy. But the residual errors show that these limits as well as those of Fowler are too large. The cause is probably due to the fact that the first line is not the calculated S(1) but the observed P(1). They never exactly agree.

In the case of D and F series, I feel some doubt as to whether the actual lines follow a given formula sequence, although it may be possible that they are in some way related to such typical sequences. There can be little doubt, I think, but that the values of the wave numbers are determined by an expression of the general type $A-B/D^2(m)$ but the denominator

certainly cannot itself be a mathematical function of the integer m for both the D_{11} and D_{12} lines, or for both the P_1 and P_2 lines. They are best discussed by calculating the actual values of D(m) from the observed wave numbers, and then attempting to investigate the relationships between them. This is the method adopted in (III) and it will be followed in the present note.

The values of δ for the elements in question are (III, pp. 344-346)

Mg.	Ca.	Sr.	Ba.	Ra.
21.48	58.14	277.89	$683 \cdot 2$	1853-16

The theory that the separations of the S, D, and P series depend on multiples of the oun, and that the satellite separations of the D, and consequently the F separations, also depend on other multiples of the same quantity, can, I think, be considered as established, and may be taken as a test for new cases. This part of the discussion will then be taken first.

The exactness of the determination of the denominator differences which produce the observed separations depends almost wholly on the exactness of the separations as measured, and only slightly on the true value of the limit. In fact the value of the difference is affected by the same percentage error as the value of the separation adopted. Any error in the limit produces only a small effect, because it enters as the difference of two numbers each affected by nearly the same errors. To illustrate this point the calculation is given for Ca, and the results only for the other elements.

Fowler quotes for Ca a doublet separation $\nu=223\cdot0$ and limits $70289\cdot2$ for S_1 and $70512\cdot2$ for S_2 . Take the true limits as being ξ greater and that the value of $\nu=223\cdot0$ is affected with an error $d\nu$. Using the numerator 4N, the denominators for these limits are respectively $2\cdot498012-17\cdot77\xi$ and $2\cdot494060-17\cdot68\xi$. The difference of these digits, allowing for the error in ν , is, therefore,

$$3952 + 17.7 dv - 0.09 \xi$$

In this $d\nu$ will be less than 0.1, and unless the value of the limit is very much in error the true difference cannot differ from 3952 by more than 2 units in the last place. Now δ for Ca is 58.14, and $68\delta = 3953.5$. The possible error in δ is probably much less than one per thousand. These numbers agree easily within any possible observation errors, and we may say that the separation is due to a denominator difference $\Delta' = 68\delta$. In (III), Δ_1, Δ_2 , have been used to denote the corresponding values in the triplet series, and Δ for $\Delta_1 + \Delta_2$. In order to have a consistent notation we might denote the multiplicity of the series by a corresponding dash and write respectively Δ_1'' , Δ_2'' , Δ'' for triplets (or two separations) and Δ' for doublets. The same notation might be extended to the series themselves, thus CaS₁''(3) would VOL, XCL.—A.

refer to the triplet system and CaS₁'(3) to the doublets now being considered.

For the other elements Mg, Sr, Fowler's values for $S_1(\infty)$ are respectively 85479.8 with $\nu=91.5$ and 64323.3 with $\nu=800$. But 800 is much too small, and is due to an arithmetical error in deducing the wave number from the wave length 4215.66. The least square value weighted by possible errors is 801.24. Adopting this we have denominator differences

```
for Mg 1211 - 13 \cdot 2 d\nu - 0.02 \xi, 56\frac{1}{2} \delta = 1213, for Sr 16113 - 20 d\nu - 0.37 \xi, 58 \delta = 16117.7.
```

Hence clearly for Mg $\Delta' = 56\frac{1}{2}\delta$ and for Sr $\Delta' = 58\delta$, noting that $d\nu$ cannot be more than about 0.1.

Fowler has drawn attention to the difference between the behaviour of Mg and the other elements as showing no line corresponding to negative values in the Diffuse. A similar difference is shown also in the triplet series (III, p. 356), and seems to show that Mg is more analogous to the low melting point elements of this group (Zn, etc.) than to the earths. This difference is exemplified also when the atomic volume term is considered as is done below (p. 462).

Passing on to the second law, the separations of the satellites in the Diffuse series are caused by denominator differences in VD_{11} and VD_{12} . That for the first set is always greater than for succeeding sets, for which latter they are in many cases, though not always, the same. Moreover they are generally multiples of δ_1 . The calculated results are here affected by observed errors in the single lines, but again are almost independent of the limit error. The results are of course independent of any formulæ beyond the fact that the wave number is of the form $\Lambda-4N/D^2$.

The values of the denominators are given in Table I. The figures in brackets denote possible errors, and as the effect of the change of limit is practically the same for D_{11} and D_{12} it is only entered for the first.

Mg shows no satellites, as is the case also in its triplet series.

The corresponding numbers for Ba and Sr are also placed in this Table from the discussion given below.

In order to obtain the corresponding quantities in Ba and Ra it will be necessary to make a digression to discuss the enhanced series in general in these elements.

Ba.—Ritz gave for the S series the lines -4554.21, -4934.24; 4900.13, 4525.19; 2771.51, 2647.41; to which Saunders* has since added 2287, 2202. The Zeeman effects for the first two pairs have been observed and the

^{* &#}x27;Phys. Rev.,' vol. 28, p. 152.

Table I.

	(Ca.	
	$\Delta' = 3953.$	δ == 58 .14.	
2 ·812876 (10) — 14 ·2 ξ 47320 — 29 ξ	858	2 · 312018 (14)	$59\delta_1 = 857.6$
8 ·360196 (18) — 48 ·2 ξ 8811 — 52 ξ	830	8 -859866 (18)	$57\delta_1 = 828.5$
4 ·869007 (P) -95 £ 3972-81 ·7 £	799	*4 ·3682 08 (?)	$55\delta_1 = 799.4$
5 · 872979 (7) - 170 · 7 ξ 5807 - 120 ξ			
6 ·378886 (?) — 296 ξ	* Calculated	l from Do-v.	

The satellite differences are therefore 59 δ_1 , 57 δ_1 , 55 δ_1 , although, as the third line probably has large observation errors, the 55 81, in spite of its exact agreement with the observed separations, may be 54, 56, or even the same as for the second line. The denominator difference for m=5and 6 is so excessive as to throw some doubt on the allocation of the last to $D_{11}(6)$.

The satellite differences are therefore $60\delta_1$, $62\delta_1$, $60\delta_1$. The values for the second and third are not so close as in Ca, but are both within error limits.

	Ba		
	$\Delta' = 38610$.	$\hat{c} = 683 \cdot 2.$	
2 ·421304 (?) - 16 ξ 148328 - 35 ·8 ξ	14234 - 0·3 [≤]	2 ·407070 (5)	$83 \tilde{c}_1 = 14176 \cdot 4$
3 ·569t82 (15) - 51 ·8 \$ 35512 - 59 \$	10602 - 0 ·4 ξ	3 ·559030 (15)	$62\delta_1 \approx 10589.6$
4 1605144 (80) - 111 ξ 17506 - 91 ξ	10529 − 0·5 ξ	4 *594615 (80)	628,
5 ·622650 (2000) - 202 ξ • 18006	8087	5 ·614563 (2000)	
6 · 64 0656 (?)	T		
	$\Delta' = 112116.$ Ra	$\delta = 1853 \cdot 16 + e.$	
2 ·465091 — 146708 —	35662-	2 ·429429	$778_1 = 85673$
8 ·611799 — 58814 —	26376	8 *585423	$57\hat{e}_1 = 26407 + 57e$
4.670013			

Zeeman patterns are those for a doublet S series. The doublet separation There can be no doubt but that the allocation is correct and also that they form an enhanced series. The formula calculated from the 2nd, 3rd, and 4th is

$$n = 58622 \cdot 8 - 4 N/(m + 0.477659 - 0.270245/m)^{2}.$$

This reproduces the first with an error -143. The limit may be taken as probably correct within ± 50 . The two limits are then $58622.8 + \xi$ and 1690.63 additional or $60313.43 + \xi$. These give a denominator difference

$$38610 - 0.98 \, \xi + 22.35 \, d\nu = 56\frac{1}{2} \, (683.3 - 0.01 \, \xi + 0.4 \, d\nu).$$

Now, for Ba, $\delta = 683.2$ with an uncertainty of about unity in the fourth digit Hence $\Delta' = 56\frac{1}{2}\delta$.

For the Diffuse series we take the following set-

	λ.	n.		
-(10) 5858 91	-17077 ·96 (0 ·29) -16190 ·58 (?)	887 43	
- `	6148 6	-16190 58 (?)	007 20	1690 .59
	6497 .07	-15387 37 (0-24)		
) 4166 '24	28995 :83 (0:29)	205 41	
(8	4180 88	24201 ·24 (0 ·29)	200 41	1690 ·97
(6	8891 97	' 25686 ·80 (0 ·83)		
(4	2641 .52	37845 ·97 (0 ·72) 37940 ·87 (0 ·72)	04.00	
(8)	2634 91	37940 ·87 (0 ·72)	94 .90	1690 ·66
(ō	2528 .60	89536 ·68 (P)		
	2236	44709 (? 10)	40	
•	2234	44749 (? 10)	40	1680
	2155	46389 (? 11)		
	2054	48689 (?)		
	1987	50812 (F)		

In the first set, the D_{11} line (6148) is taken from an observation by Moore* in the course of his investigation of the Zeeman effect in the Ba spectrum, and it was strong enough to enable him to determine its Zeeman pattern. There can be little doubt as to the allocation of the first two sets, as they both show the Zeeman patterns for diffuse doublets. It is curious, however, that the D_{11} of the first should be so much weaker than the D_{12} , which is abnormally strong. It would seem that only a small proportion of the configurations which give the normal line D_{12} are split up and laterally displaced (III) to the D_{11} set. As a rule they appear to be less stable than those giving D_{11} . It will be seen later that a similar effect is shown by Ra.

In the third set D_{21} (2528) is a line observed by Exner and Haschek. The other lines in the first three sets are measures of Kayser and Runge, whose estimates of possible errors, translated to wave numbers, are inserted in brackets after the measures. The remaining lines are by Saunders (loc. cit.). Using the limit for $S(\infty)$ and the second and third lines, the formula for D_{11} is

$$n = 58622.8 + 4N/(m + 0.711680 - 0.426144/m)^{2}.$$

This gives $\lambda = 2233$ for m = 5, which is Saunders' 2234, and $\lambda = 2054.5$ for m = 6, which establishes the set. The denominators are given in Table I. It is seen that the denominator difference for the first satellite is close on $83\delta_1$, but the difference between $83\delta_1$ and the observed is too large to give so satisfactory a decision as in other cases. This, however, may well be due to the unknown observation error in D_{12} . This line was not observed

by Kayser and Runge, but incidentally by Moore in the course of his investigation of the Zeeman phenomenon. The error in D₁₂ cannot be larger than 5, and if the whole error be thrown on D₁₁ the denominator should be 58 less. Other considerations given below (p. 463) confirm this, and at the same time show that the limit should be about 3 larger. The wavelength of the line should be about 1 Å.U. less than that measured, and make the satellite separation 883.8.

Ra.—The case of Ra is more difficult as the spectrum has not been measured above 6640 nor below 2700. Moreover, with increasing atomic weight the radiating configurations appear to get more unstable and to break up into numerous others, with the consequent disappearance of regularities. By far the best measurements are those of the spark spectrum by Runge and Precht.* Their plates were not sensitive above 6500. Haschek observed a few above this. Ritz (loc. cit.) gave for the S series the two sets -(100) 3814·578, -(50) 4682·359, and (15) 5813·85, (10) 4533·327. These give doublet separations respectively of 4857.00 and 4857.16. these may be added for D(3), (20) 4436.489, (50) 4340.830, (50) 3649.748. These selections are probably correct—although we have not their Zeeman patterns as in Ba. They are not sufficient, however, to determine the limits unless a Rydberg formula were exact, in which case the two S lines would be sufficient. But in the other elements limits as thus found are about 1800 too high, and thus quite inadmissible. We are, therefore, driven to apply the method which is used in (111, p. 405) in studying the spectrum of The Rydberg limit from the two S lines is about 57863. analogy with the other elements the real limit should be about 1800 less, or in the neighbourhood of 56000. It should be such that the value of Δ' required for the observed separation (4857) is a multiple of the oun of δ_2 from analogy with the others—and that the difference for the satellite separation (496.55) of D(3) should also be a multiple. If the first condition is applied, a series of values for the limits are obtained. Using these, they are tested for the second condition. It is found that one alone satisfies it, and this is then taken as the real limit.

In order to apply this method it is necessary to know beforehand the degree of accuracy of which the data are susceptible. These data are respectively the values of δ , ν , and the satellite separation. For Ra $\delta = 1853 \cdot 16 + e$, where e is probably less than 0.5, or say 1 in 3700. For the other data it is necessary to know the possible errors of observation, which unfortunately Runge and Precht do not give. But they give readings for the special lines in question to the third decimal place $(S_1(3) \text{ excepted})$.

We shall probably be safe, therefore, in assuming that these are not in error by more than 0.005 Å.U. For $S_1(3)$, which is a good line, we may take 0.05 Å.U. With these the following values of ν are obtained*:—

```
S (2), 4857 \cdot 00 - 0 \cdot 034 p + 0 \cdot 023 q,
S (3), 4857 \cdot 16 - 0 \cdot 147 p' + 0 \cdot 024 q',
D (3), 4857 \cdot 34 - 0 \cdot 037 p'' + 0 \cdot 025 q'',
```

in which p and q must lie between ± 1 . It is clear that the Diffuse and Sharp separations cannot be exactly the same if our error limits are correctly assumed. Those of S(3) and D(3) may be equal, and as S(2) is possibly really P(1) its smaller ν is in apparent agreement with indications in other series. In any case they do not differ by an amount sufficient to affect the determination of the satellite difference. The S(∞) will, therefore, be determined by $\nu = 4857.05 \pm 0.05$.

The satellite separation, with the same supposed observation errors, is 496.50 - 0.026p + 0.025q, or say 496.50 ± 0.05 .

Between 57863 and 55000 nine limits were found which satisfied the first condition. The values of the denominator difference ran from 59 δ to 63 δ . These were tested on D(3). They all distinctly failed to satisfy the condition except that due to $60\frac{1}{2}\delta$. This belonged to limits $56653\cdot23$ and $61510\cdot28$. Taking the actual limits to be ξ larger, the denominator difference is $112116-2\cdot85\ \xi=60\frac{1}{2}\ (1853\cdot157-0\cdot047\ \xi)=60\frac{1}{2}\ \delta$. With the assumed maximum values of e above for δ , ξ can vary only by ± 10 . This limit value is now used for D(3), only ξ will be slightly different if the ν for D is $4857\cdot37$. The denominators for D₁₁(3) and D₁₂(3) are now $3\cdot611799$ and $3\cdot585423$. The difference is $26376-1\cdot2\ \xi-262\ (d\lambda-d\lambda')$, where $d\lambda$, $d\lambda'$, are the errors in observed D₁₁ and D₁₃. Now $57\delta_1=26407+57e$. If these are to be equal $31+57e=-1\cdot2\ \xi-262\ (d\lambda-d\lambda')$. This equality can be met by values of e, ξ , $d\lambda$, $d\lambda'$ well within their maximum possible errors assumed above. We are justified, therefore, in taking $\Delta'=60\frac{1}{2}\delta$ and the limit $S_1(\infty)=56653\cdot23$.

The D(2) set of lines should be in reverse order in the red. As no separation 4857 occurs there amongst observed lines, at least D₂(2) is outside the observed region, but it may still happen that the lines D₁₁(2) and D₁₂(2) are within. If so, their denominator difference should be a multiple of δ_1 and their mantissæ considerably less than the corresponding ones for D(3). Also the lines should be strong, and from analogy with the other elements the satellite separation should be rather greater than four times that for D(3). There are

^{*} There are several other lines with the same separation, but it will be safer to deal only with the S and D lines.

two such lines in Runge and Precht's list, viz., (10)5660·81 and (4)6439·1. The latter is very close to the limits of sensitiveness in the red of Runge and Precht's plates, and consequently the line itself must be considerably stronger than is indicated by a plate intensity of 4. Their separation is 2134·61, rather larger than 4×496 and they occupy positions in step with those of Ba. Taking their wave numbers $D_{12} = -17660·51$ and $D_{11} = -15525·90$, their denominators are $2 \cdot 429429$ and $2 \cdot 465091$. Their difference is, therefore, 35662 and $77\delta_1 = 35673 + 19c$, the same within error limits. The ratio for the first and second sets, 77:57=1.35, is practically the same as for Ba, 83:62=1.34. Moreover it is noticeable that they show precisely the same abnormality as in Ba, viz., the $D_{11}(2)$ is of less intensity than the satellite $D_{12}(2)$. There is also further evidence in that the denominators of the corresponding lines for m=2 and 3 differ very closely by multiples of δ_1 —a result shown by all other known Diffuse series (see 111, Table 11). Further we should expect F series with a separation 2134·61. Evidence for this is given below.

The set for m=4 will be in the ultra-violet. The shortest lines given by Runge and Precht with $n=35528\cdot 5$ and 36900·7 are strong. But the former gives a denominator with a mantissa smaller than for m=3, and the latter one with a value much higher than analogy with other spectra would lead us to expect. Exner and Haschek give a spark line at 2736·20 with $n=36547\cdot 04$. This gives a denominator 4·670613, with mantissa 58814 above that for m=3, which again is 146708 above that for m=2. It is therefore, in fair order of magnitude. The difference 58814 should be a multiple of δ_1 , but it is affected with an observation error of 1548d λ . With $d\lambda=0.05$, this is 77. Now $127\delta_1=58828$, and as $\delta_1=465\cdot 3$, even the large possible error of 77 could not alter the multiple. It is quite possible, therefore, that $\lambda=2736\cdot 20$ is $D_{11}(4)$; the satellite is too faint to have been observed and $D_2(4)$ is outside the region of observation. If, as in Ba, the satellite differences for m=3 and 4 are the same, these unobserved lines would be at 2752·7 and 2428·0, and the satellite separation would be 229·3.

The first three sets of RaD as thus arranged are therefore

λ.	я.		
5660 .81	- 17660 ·51	2134 ·61	
6489 ·1	- 15525 ·90	2104 01	4857 00
[-7808 2]	[-12808.51]		
4486 489	22534 ·16	496 ·55	
4840 .880	23080 71	700 00	4857 ·34
8849 748	27391 50		
[2752 7]	[36317 -78]	19.000	
2786 20	86547 04	229 31	4857 .00
[2428 0]	[41174 .73]		

The results obtained for Δ' and the satellite differences are collected in Table II. For purposes of comparison the values of $\Delta = \Delta_1 + \Delta_2$, and of the satellite differences for the triplet series, are also added.

'i'a	hla	11
1 a	D10	11.

İ		Δ'.	Satellites.	
	Δ.		Triplets.	Doublets.
Мд	598	561 ខ	None	None.
Сы	71 <u>1</u> 8	683	Multiples of δ. { 18δ, 18δ, 14δ 8δ, 8δ	Multiples of δ_1 . 59 δ_1 , 57 δ_1 , 55 δ_1
Sr	62 1 δ	583	{ 188, 128, 158, 158, 158	6681, 6281, 6081
Ва	6012	56 <u>1</u> 8	{ 148, 108 118, P	8381, 6281, 6281
Ra	684 8	6048	{ ⅓8, ⅓8 28	7781, 5781

In general Δ_1 is a little greater than $2\Delta_2$ and Δ' less than $3\Delta_2$. Thus

	Δ ₁ .	Δ'.
Mg	24. + 55,	342-551
Ca	$2\Delta_{2} + 4\delta_{1}$	3 A2 10 81
8r	$2\Delta_{2} + 10\delta_{1}$	34-48
Ba	2 4 + 82 8	$3\Delta_2 + 16\delta_1$
Ra	*2 A, +528,	84. +208

[&]quot; A2 is doubtful in Ra.

The F Series.—In the F series as given by Fowler the separations are both larger than in the D satellites, for instance 65 as against 596 in Ca, and 2848 as against 2792 in Sr. The differences are too large and too systematic to be ascribed to observation errors. They seem to be constant for the different orders, which would point to displacements in the limits if they are really the F lines or they are not the normal F lines. Now pairs exist with the proper separation. Again the discussion of the D series has shown that in Ba the F separation should be 887, or more probably 884, and that in Ra, if the suggested values for D₁₁, D₁₂ are correct, a separation of 2134 should be expected. These are found, and homologous sets can be found in all four spectra with the true F separations and in which the Zeeman pattern of one of each set (Ra excepted) has been given by Moore (loc. cit.) and is the same for

the three. But these lines are also closely connected in the same manner in each spectrum with the triplet F series. The clearing up of this connection should probably throw a great deal of light on the connection of the various series, but it will require much further investigation. The discussion is therefore held back for the present. As bearing on the correctness of the identification of the Ra D(2) lines, however, the following lines—in addition to D_{11} and D_{12} —show the separation to be expected.

λ.	n,	
4692 1	21306 .56	2133 ·06
4265 ·1	23439 -62	
4740 -3	21089 93	2132 45 2142 94
4305 0	23222 ·38	
3941 :3	25865 :32	

Of these one is probably negative and corresponds to m=1, the other to m=2.

The laws relating to the dependence of the separations of doublets, triplets, and satellites on the oun may be considered so well established that they can be used as tests for new theories. The foregoing discussion thus affords strong testimony in favour of Fowler's explanation. We may now use these new series as tests for certain other relations, which, although perhaps they cannot be considered as proved, yet have a considerable body of evidence in their favour.

(1) We will take as the first of these, the relation that the denominator of the first term of the p-sequence—that which in the alkalies gives the P series—is proportional to a multiple of the atomic volume. It would appear that there is in connection with each atom a fundamental quantity, of the nature of a volume. It is roughly proportional (probably to about 2 per cent.) to the atomic volume as measured by the ratio of the atomic weight to the density of the substance in the solid state, a measure which is dependent to some extent on temperature and other effects. The law would state that the mantissa of the denominator of the first-line should be kxv, where v is the atomic volume, x a whole number, and k a number in the neighbourhood of 0.002740, this number being probably correct to about 2 per cent. The difficulty in determining its value more accurately depends on the facts that the true value of v is not known within that percentage and to the uncertainty as to whether the fractional part of the denominator itself follows the law, or whether there is some group constant to which the term is added. But, if so, this constant is so near unity that it is quite possible to determine whether the multiple exists—and in that case its value—without ambiguity, allowing the factor to be 0.002740 $(1\pm1/50)$.

In the alkalies the p sequence gives the P series and consequently **vol.** xci.—A.

 $S_1(\infty) = p_1(1)$, $S_2(\infty) = p_2(1)$. It is easiest, therefore, in this case to apply the test to the limits of the S and D series. It would appear that the p_2 sequence is of a more fundamental type than the p_1 , as is also the case in the Diffuse satellites in which the outer satellite is the real normal line from which the more intense D₁₁ lines are formed by lateral displacement. Here $p_1(1)$ is formed from $p_2(1)$ by adding Δ . In certain other cases it would appear that the Sharp series depends on the p sequence and the Principal on the s sequence. In this case we look for the presence of the law in VS(2), which is p(1). This is apparently the case in the triplets of Group 2. The values of the multiples for the elements already tested are given in (III, p. 47). In the present case, then, both $S_2(\infty)$ and the VS(2) must be tested. result is that Mg follows the law in VS(2) and not in $S_2(\infty)$. On the contrary, in Ca, Sr, Ba the law is followed in $S_2(\infty)$ and not for VS(2). The densities used are the same as in (II), viz., Mg(1.72), Ca(1.57), Sr(2.50), Ba (3.77). The results are given in the following table:--

```
Mg. Mantissa of VS(2) = 920434 = 065050 v = 002710 \times 24 v. Ca. , S_2(\infty) = 494040 = 019336 v = 002762 \times 7 v. Sr. , = 595175 = 016968 v = 002828 \times 6 v. Ba. , = 696694 = 019110 v = 002730 \times 7 v. Ra. , = 670322 = 002961 \rho v = 002740 x v. With density of Ra = \rho = 0.94 x.
```

The greatest deviation is shown by Sr, in which the density determinations by different observers vary greatly. It is clear that these enhanced series support the truth of the law at least as a first approximation. If Ra is supposed to behave like Ca, Sr, Ba, its density must be 0.94x, where x is an integer. From analogy it would be 6 or 7, giving a density of 5.64 or 6.58. A corresponding theory applied to the triplet series (II, p. 46), in which the numbers are less definite, gave $\rho = 1.02x$ with x = 5 or 6.

(2) Apparently the Diffuse sequence depends on multiples of the oun in a similar manner to that in which the p sequence depends on the atomic volume. In a very large number of cases the denominator of the outermost satellites of the first set is a multiple of the Δ , and in all other cases the difference between the denominator and the nearest multiple of Δ is itself a multiple of the oun. In the latter case the nature of the evidence for low atomic weights is not decisive as in them the oun is so small that it is easily smothered by observation errors. In the present discussion, then, the question to be tested is whether the first satellite denominator is a multiple of Δ , or differs from such multiple by a multiple of the oun. In the case of Mg the Δ is too small to settle the question one way or the other.

Ca, using Paschen's value of $\lambda = 8542.6$ —

For D₁₂, mantissa =
$$312038(10) - 14.1\xi = 79(3949 - 18\xi) = 79\Delta''$$
, with $\xi = -20$.

Sr, using Randall's value of $\lambda = 9958:31$ —

For D₁₂, mantissa =
$$\cdot 429954$$
 (?) $-16\cdot 4\xi$, is not a multiple of Δ' .
For D₁₁, ... = $\cdot 434527 - 16\cdot 4\xi = 27 (16093\cdot 6 - 6\xi) = 27\Delta'$.

If, however, the limit be determined from the second, third, and fourth lines—which is generally to be preferred—it comes out 49 lower. To make the mantissa an exact multiple, the limit should be lower by 32·3, and probably also more correct than $\xi = 0$. It is curious that Sr shows precisely the same kind of displacement in the triplet system, the exact multiple being there found in D_{12} instead of in D_{13} .

Ba.—Here neither D_{11} nor D_{12} give multiples of Δ' , but they differ from such by multiples of the oun.

For D₁₂, mantissa =
$$\cdot 407070(5) - 15 \cdot 9 \xi = 11 \Delta' - 103 \delta_1 - 48 - 16 \xi$$
.
D₁₁, = $\cdot 421304(?) - 16 \xi = 11 \Delta' - 5 \delta + 10 - 16 \xi$.

Now it was seen above in considering the satellite separations that D_{11} with a large possible error makes the denominator too large by 58. This corrected value would give for D_{11} above

Mantissa =
$$421246 - 16\xi = 11\Delta' - 5\delta - 48 - 16\xi$$
.

Ra-

For D₁₂, mantissa =
$$429429 (51 d\lambda) - 16.3 \xi = 4\Delta' - 41 \delta_1 - 36 - 16.3 \xi$$
.
D₁₁, " = $465091 (41 d\lambda) - 17 \xi = 4\Delta' + 9\delta - 48 - 17 \xi$.

With $\xi = -2.5$ the relations hold, within small observation errors, for both.

As to the changes in the limits required by the above values of ξ , it is to be noted that for Ba and Ra they should not be large, because if the theory used to determine the Ra limit is correct the value obtained must be close to the real value—and —2.5 is quite allowable. For Ba the limit is obtained from the second, third, and fourth lines and is a better value therefore than that obtained from the first or fifth. Fowler's limits for Ca and Sr are on the face too large, as the O—C for the later lines show. Hence, here again the evidence of the enhanced series gives weighty support to a relation obtained in (III) from a study of other series.

Gaseous Combustion at High Pressures.

By WILLIAM ARTHUR BONE, D.Sc., F.R.S., in collaboration with Messrs. Hamilton Davies, B.Sc., H. H. Gray, B.Sc., Herbert H. Henstock, M.Sc., Ph.D., and J. B. Dawson, B.Sc.

(Received December 22, 1914.)

(Abstract.)

The paper gives an account of investigations on gaseous combustion under high pressures carried out in the Fuel Department of the University of Leeds during the years 1906-12, with a special installation of apparatus, the cost of which was defrayed out of grants made from time to time by the Government Grant Committee.

Experiments in which mixtures of methane with less than its own volume of oxygen were exploded in steel bombs at initial pressures of between 8 and 32 atmospheres have given results in harmony with the "hydroxylation" theory of hydrocarbon combustion put forward some years ago by Prof. Bone. The influence of various secondary reactions upon the products of the primary oxidation whilst the gases are cooling down after the attainment of maximum pressure is discussed in the light of the experimental results.

Results of experiments upon an equimolecular mixture of ethane and oxygen, whose behaviour is crucial in respect of the different views of hydrocarbon combustion advanced in recent years, have again confirmed the hydroxylation theory. Another section of the paper deals with an experimental determination of the relative affinities of methane, hydrogen, and carbon monoxide for oxygen in flames. It is shown (1) that the affinity of methane is at least twenty times as great as that of hydrogen, and (2) that when mixtures corresponding to $CH_4 + O_2 + xH_2$ are fired under high initial pressures, in which the partial pressures of methane and oxygen are kept constant and x only varied, the distribution of oxygen between the methane and hydrogen varies with x^2 , a circumstance which means that hydrogen is burnt directly to steam in flames as the result of the trimolecular change $2H_2 + O_2 = 2H_2O$, and not (as some have supposed) indirectly through, hydrogen peroxide.

The affinity of carbon monoxide is shown to be comparable with that of hydrogen for oxygen in flames. Experiments are also described in which mixtures of ethylene, oxygen, and hydrogen, corresponding to $C_2H_4 + O_2 + xH_3$.

were exploded at high initial pressures; inter alia it was found possible to increase x up to 8 without causing any deposition of carbon on explosion. The theoretical bearing of the results is fully discussed.

The final section of the paper describes experiments in which the whole pressure curves, up to and far beyond the attainment of maximum pressure, were recorded when mixtures corresponding to (1) $2H_2 + O_2 + 4N_2$, (2) $2CO + O_2 + 4N_2$, and (3) $CH_4 + O_2 + 4N_2$, are exploded under initial pressure of about 50 atmospheres. It is shown that the rates of attainment of maximum pressure in each case have no direct relation to the order of affinities of the various gases for oxygen.

Electrical Effects accompanying the Decomposition of Organic Compounds. II.—Ionisation of the Gases produced during Fermentation.

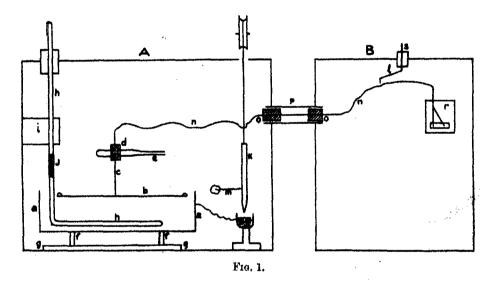
By M. C. Potter, Sc.D., M.A., Professor of Botany in the University of Durham.

(Communicated by Dr. A. D. Waller, F.R.S. Received February 26, 1915.)

It is well known that the gases liberated during certain chemical actions carry charges of electricity. Thus Lavoisier and Laplace found that the hydrogen liberated from the action of hydrochloric acid upon iron is charged positively. More recently Enright (1) has noted the same effect, and Townsend (2) has shown that the gases liberated during electrolysis are also charged. In a previous paper (3) evidence has been brought forward to show that the decomposition of organic matter gives rise to electrical effects which are of the same nature as those produced by the action of acids upon metals. It seemed therefore an interesting point to investigate whether the CO₂ escaping from the fermentation of a saccharine solution might carry an electric charge and be ionised.

To determine this point a series of experiments were carried out by the employment of a gold leaf electroscope and a Dolezalek electrometer. The method adopted was to suspend a metal plate with rolled edge a few centimetres above the surface of glucose undergoing fermentation through the action of yeast, the metal plate being connected with the electroscope or electrometer, and the whole suitably screened in a box lined with tinfoil. Readings were then taken in the ordinary manner.

Description of the Apparatus (fig. 1).—To avoid, as far as possible, the large accumulation of froth which always accompanies alcoholic fermentation, the fermenting glucose was enclosed in a shallow tin dish (a), 25 cm. in diameter and 7 cm. in depth, the large free surface permitting the CO2 to escape more freely. For the purpose of insulation the dish was supported upon three amberoid plugs (f) fixed in a wooden base (g), the key (k)providing the means of earthing the dish, if required, through the earthed wire (m). The metal plate (b), 22.5 cm, in diameter, was suspended by a copper wire (c) soldered to its upper surface, this copper wire passing through a sulphur plug (d) held firmly in a support (e). This portion of the apparatus was enclosed in a light wooden box (A) lined with tinfoil and



having a detachable front also lined with tinfoil. By this means the fermenting glucose and accessory apparatus were effectually screened from external influence.

Attention has already been drawn to the well known fact that the CO. evolved during fermentation does not escape freely from the fermenting liquid, and thus it is necessary to provide some means of stirring the yeastglucose solution. This was accomplished by means of a glass rod (h) bent at right angles (with a short rod of ebonite (j) inserted for insulation) and fixed to the inside of the box (A) by passing through the support (i), the lower portion being held horizontally just above the bottom of the dish and immersed in the fermenting liquid. The upper end of this rod projected through a small hole in the top of the box, and by turning the projecting

piece backwards and forwards the liquid in the dish could be stirred without disturbing its insulation.

The electroscope (r) employed was of the ordinary type, with a gold leaf measuring 4.5 cm. in length by 1 mm. in breadth. This was enclosed in a brass box with windows, protected by glass slips, cut in opposite sides for the observation of the gold leaf, sulphur being used for insulation. The electroscope was screened by a wooden box (B) lined with tinfoil, similarly to the box A. It was charged from a battery of 220 volts by a bent wire (l) which passed through the sulphur plug (s) fitted into a hole in the top of B. A convenient and inexpensive battery was contrived by connecting in series a number of "refills" used for electric torches. Such a battery of 150 cells gave an E.M.F. of 220 volts, which remained constant for a considerable time. The boxes A and B were carefully earthed and connected by a metal tube (p), through which passed a copper wire (n) insulated by the amberoid plugs (o), the copper wire serving to connect the electroscope with the metal plate.

The movement of the gold leaf was observed by means of a horizontal microscope with a micrometer eyepiece. It was found that five scale divisions of the eyepiece corresponded to a difference of charge of 4.4 volts upon the electroscope and plate. The times at which the gold leaf passed over the divisions were taken by means of a stop-watch. During each series of observations the times were noted for the fall of the gold leaf over the same divisions, which could readily be effected, as both the electroscope and plate were charged from the battery of 220 volts.

Before commencing any series of observations the insulation was carefully tested, especially that of the ebonite (j) inserted in the stirrer, which was rubbed with glass paper to ensure a clean surface.

For the glucose solution 100 grm. of ordinary commercial glucose were dissolved in one litre of water, and the solution was placed in the box A for some hours that it might acquire the same temperature as the box and its contents. About 800 c.c. of this solution was then poured into the tin dish, the metal plate was placed in position, and a series of readings taken to determine the rate of leak of the gold leaf. To the remaining 200 c.c. was added approximately 100 grm. of commercial pressed yeast to start the fermentation. When the rate of leak had been determined the 200 c.c. containing the yeast was added to the solution already in the tin dish and readings were taken for the fall of the gold leaf under these conditions.

As the result of many observations it was found that when the dish contained glucose solution without yeast, the rate of electroscope leak was uniform over the same five scale divisions of the eyepiece, whether the electroscope was charged positively or negatively, and this rate of leak was uninfluenced by the action of the stirrer in the glucose. That is the curve representing the rate of leak is a straight line, The way was therefore clear for further advance.

The general plan of the experiments was to introduce the glucose and yeast in the manner just described, adjust the metal plate so that it would be suspended approximately 4 cm. above the surface of the fermenting glucose and concentric with the dish, then connect the metal plate with the electroscope and charge them to the standard voltage (220), recharging after each reading. Owing to the necessity of stirring the glucose, the readings to determine the rate of leak of the electroscope were taken in sets of three, one immediately after the other: that is one reading before stirring ((I) in the diagram), one during which the stirring was in operation (II), and a third in which no stirring took place (III).

Experiments with the Electroscope.

Two sets of observations were required, viz. the electroscope and plate charged positively, and the electroscope and plate charged negatively. In each case the disc containing the fermenting glucose was connected to earth.

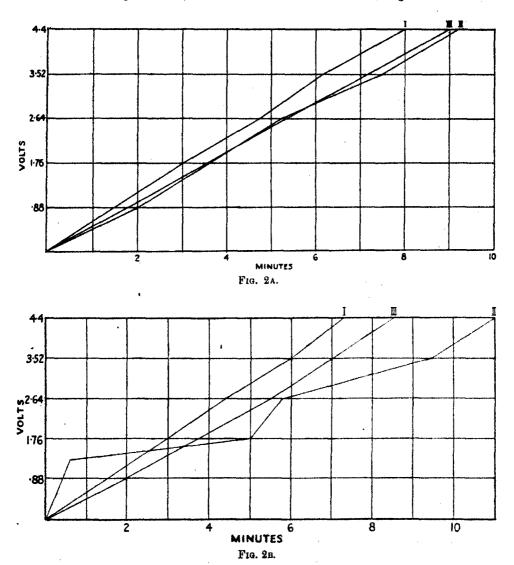
Electroscope and Plate Charged Negatively.—An example typical of many observations is shown in the diagram, fig. 2A and B. The curves in A refer to readings taken almost immediately after the introduction of the yeast, and before the full rate of velocity of the fermentation had been reached. The times are plotted horizontally in minutes and the divisions of the eyepiece vertically. The curves I and III are practically straight lines, and show that the rate of leak in the absence of stirring is uniform. It will be noted that in III, after the stirring, the rate of leak is slower than in I. In II the curve is slightly bent, but as there is little evolution of CO₂ at such an early stage the curves do not exhibit any very perceptible difference.

The three curves in B represent readings taken later than those in A, at a time when the fermentation would be actively proceeding. Some 17 minutes elapsed between the curve II in B, and the corresponding one in A, and during this interval a large quantity of CO₂ would be formed and not liberated from the fermenting solution until stirring took place.

Curves I and III are again straight lines, but the times occupied by the gold leaf passing over the five divisions are somewhat faster than was the case in A. The curve III also again shows a decreased rate of leak as compared with I, owing no doubt to the liberation of the entangled CO₂ during the process of stirring.

Curve II shows in a marked degree the sudden evolution of the CO₂ due to the action of the stirrer. At the commencement of the

stirring the entangled CO₂ rapidly escaped, and simultaneously the gold leaf fell through one and a half divisions in 36 seconds, a great contrast



to the rate of leak in I and II, when the time occupied for the leaf to fall over the first division was 1½ and 2 minutes respectively. After the sudden ebullition of the CO₂, due to the action of the stirrer, the stirring was stopped, and the fall of the gold leaf then became very slow, taking 4 minutes 24 seconds to reach the next division. During

this time CO₂ would accumulate, and on proceeding again to stir the gold leaf fell through the next division in 48 seconds. The stirrer was now stopped again, and 3 minutes 42 seconds were occupied by the leaf in falling to the fourth division. Then on the re-commencement of stirring 1½ minutes only were occupied in falling to the last division.

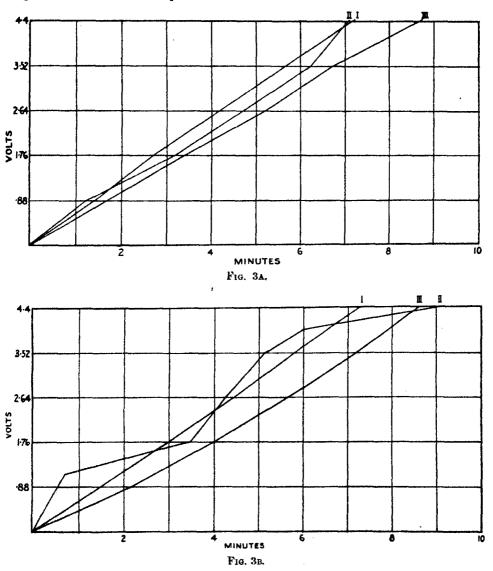
As mentioned above, five scale divisions are equivalent to a difference of 4.4 volts. Thus curve II shows that at the commencement of the stirring the electroscope and plate lost a charge of 1.32 volts in 40 seconds, in striking contrast to curve 1, which represents a discharge of 0.88 volt in 1 minute 30 seconds. During the next period (4 minutes 24 seconds), when the stirrer was not in action, the fall of the leaf was very slow, and the discharge only 0.44 volt. As soon as the leaf reached the second division, and stirring took place, the same rapid discharge of the electroscope was repeated, a discharge of 0.88 volt occurring in 48 seconds. Similarly there was again a quick discharge when stirring took place at the fourth division.

Electroscope and Plate Charged Positively.—The results obtained under these conditions (fig. 3A and B) are of the same character as those indicated when the electroscope and plate were charged negatively, and need not, therefore, be dealt with in detail. As in the latter case, the readings taken just after the introduction of the yeast (fig. 3A) show little difference between the curves I, II, and III, as there would be only a slight evolution of CO₂. But after the lapse of half an hour the effect of the escaping CO₂ is again plainly shown (fig. 3B). Curves I and III are as before straight lines, showing that approximately the same rate of discharge had been maintained. Curve II shows the rapid discharge of the needle consequent upon the action of the stirrer, then a slow rate of discharge when the stirring was discontinued, followed by a rapid discharge upon the re-commencement of stirring, and so on.

With a 10-per-cent solution of glucose there is always a considerable amount of froth, and it might be objected that the accumulation of this froth, diminishing the distance between the surface of the fermenting glucose and the metal plate, would alter the capacity of the electroscope and plate, and thus cause an error in the electroscope readings.

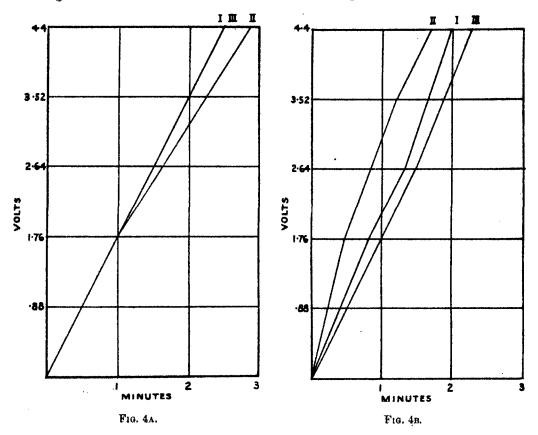
Many experiments were tried with the object of diminishing the froth, and it was found that with a 2-5-per-cent. solution of glucose it was reduced to a few bubbles and no accumulation occurred. Also with this strength of solution the fermentation proceeded rapidly, and the quantity of CO₂ evolved was sufficient to give reliable readings during the time required for each experiment. It seemed, therefore, desirable to adopt this formula for further

tests, and the following set of experiments were carried out in the same manner as the two just described, but with the employment of a 2.5-per-cent. glucose instead of the 10-per-cent.



Electroscope and Plate Charged Negatively.—In fig. 4A and B are given the curves obtained from a 2.5 solution of glucose, with approximately 100 grm. of yeast. A comparison of these figures with figs. 2 and 3 shows that with the weaker solution much steeper curves were obtained, but they retained

the same characteristics. Curves I and III are again straight lines. In fig. 4A, taken from observations made as soon as possible after the intro-

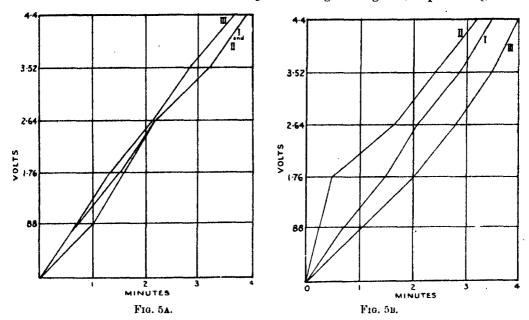


duction of the yeast, curves I and III were identical in the particular experiment here described; while curve II coincided with these in the initial stages, but after the gold leaf had passed the second division its rate of discharge was somewhat slower.

Fig. 4B gives the result of observations made some 20 minutes after the introduction of the yeast, and when its full activity had been reached. The effect of stirring is shown in curve II, the time occupied for the gold leaf to fall through the first two divisions being equal to that taken for the leaf to fall through one division in the case of curves I and III. On account of the gradient of the curves the slow rate of discharge after stirring is not a noticeable feature, but it may be remarked that the rate of fall in curve II, after stirring, is the same as in curve III.

Electroscope and Plate Charged Positively .- The curves for this experiment

with a positive charge are given in fig. 5A and B, and repeat in character the results obtained with the negative charge. Fig. 5A, representing



readings taken immediately after the introduction of the yeast, presents the same features as the other curves already given from similar observations; and fig. 5B, derived from readings after the lapse of half an hour, when the fermentation was fully established, again strikingly illustrates the sudden fall of the gold leaf as the result of stirring. In curve II the leaf fell through two divisions in 30 seconds, whereas in curves I and III it fell through one division in 45 seconds and 60 seconds respectively.

A comparison of the results obtained from the 10-per-cent. and 2.5-per-cent, solutions of glucose show that they are confirmatory one of the other. An explanation of the fact that the 2.5-per-cent, solutions give much steeper curves is afforded by the observations of Adrian Brown (4), O'Sullivan (5), and others, who found that within certain limits the amount of sugar did not influence the rate of fermentation. Slator (6), working with a definite number of yeast cells, has also shown that the rate of fermentation is practically the same from 0.5-per-cent, to 10-per-cent, solutions of glucose. The experiments with the 10-per-cent, and 2.5-per-cent, glucose were conducted at approximately the same temperature, and with roughly the same number of yeast cells per litre of glucose solution, and hence approximately the same quantity of CO₂ would be formed in equal intervals

of time. But, on account of the greater viscosity of the stronger solution, the CO₂ is in great measure prevented from escaping, as evidenced by the accumulation of froth; but in the weaker solution the CO₂ escapes more readily, and, as a consequence, the rate of fall of the gold leaf is more rapid and the curves are steeper.

Experiments with the Electrometer.

With the object of testing the results obtained with the gold leaf electroscope, a series of observations were made by substituting a Dolezalek electrometer for the electroscope in the box B. One pair of quadrants was connected to the metal plate and the other pair earthed, the arrangements otherwise remaining the same.

The dish containing the fermenting glucose was raised to a potential of 110 volts, this potential being found sufficient to produce a saturation current. The electrometer needle was suspended by a fine wire of phosphor bronze and was also maintained at a potential of 110 volts. It was found, by connecting one pole of a Clark cell to the plate and the other to the earth, that a deflection of 50 scale divisions corresponded to 1.4 volts when the needle was charged to 110 volts.

For the reasons given in the account of experiments with the electroscope, a 2.5-per-cent solution of glucose, with approximately 100 grms of yeast, was again employed as the formula from which the most reliable results could be obtained. A 10-per-cent glucose solution was also used for comparison of results, as well as a 1-per-cent.

Many trials were made with the electrometer to test the effect produced by the action of the stirrer in a solution of glucose without the addition of yeast. The stirring was found to have no influence upon the electrometer readings. The same system of reading was followed as has been previously described for the electroscope, that is: one reading without stirring, one immediately after while the stirring was in progress, and a third directly after the stirring ceased, the dish and quadrants being earthed after each reading.

The Dish and Fermenting Glucose Charged to 110 Volts Negatively.—The readings taken as soon as possible after the introduction of the yeast showed little or no difference in the rate of movement of the spot of light across the scale, whether the stirrer was in operation or not.

After allowing an interval of about half an hour for the fermentation to be thoroughly set up, it was found from many experiments that a great difference was at once noticeable between the readings taken when the stirrer was working and those immediately preceding or following. When the

fermenting glucose was left undisturbed the spot of light moved at a uniform rate, but when stirring took place it at first instantly moved rapidly over the scale and was then succeeded by a slower movement. In one particular experiment selected for illustration, 4 minutes 20 seconds were occupied by the spot of light in moving over 10 scale divisions in the absence of stirring, whereas immediately upon the commencement of stirring the spot moved quickly, eight divisions being passed over in 1 minute and the next two divisions in 1 minute 15 seconds. In the next observation, during which the medium was again left quiescent, the spot of light moved uniformly at the same rate as in the first case.

The Dish and Fermenting Glucose Charged to 110 Volts Positive.—In this case also, immediately after the introduction of the yeast, the action of the stirrer produced no alteration in the rate of movement of the spot of light. But after allowing sufficient time for a vigorous fermentation to be set up, the spot of light moved rapidly as soon as stirring commenced, reverting to a slower rate of movement after the escape of the CO₂. To cite one experiment, before the glucose was stirred it took $3\frac{1}{2}$ minutes for the spot of light to traverse 10 scale divisions, while seven divisions were passed over within one minute of the commencement of the stirring. Then following this escape of CO₂, $1\frac{1}{2}$ minutes were required for the next three divisions to be passed over.

It is thus seen that whether the fermenting glucose is charged negatively or positively the same results are obtained. That is, readings taken immediately after the addition of the yeast to the glucose solution, when fermentation had hardly commenced, show the charging of the metal plate to be influenced in a very slight degree by stirring. But at a later stage, when agitation produced a sudden liberation of CO₂, the metal plate is rapidly charged. The results obtained from the Dolezalek electrometer are in all respects in close agreement with those obtained from the electroscope.

From these experiments it may be deduced that the CO₂, when emerging from a saccharine solution, carries an electric charge or, in other words, is ionised. Also, since the electroscope is discharged, whether it be negatively or positively electrified, and as the electrometer needle is deflected, whether the fermenting glucose is charged positively or negatively, it may be concluded that both positive and negative ions are carried by the escaping CO₂.

With regard to the different times quoted in these experiments, it should be remarked that to equate the results the fermentation must be carried out with solutions of glucose of precisely equal strength, maintained at the same temperature and fermented by means of an accurately determined number of actively living yeast cells, taken from a pure culture of the same biologic form. Up to the present it has not been found possible to satisfy these necessary conditions. Nor has it yet been possible to compare the ionisation produced by yeast with a standard solution of a radium salt. The investigation goes no further than to indicate that the escaping CO₂ carries both positive and negative ions.

Lord Kelvin (7) has shown that air when bubbled through water is ionised, and this fact, as Sir J. J. Thomson (8) has pointed out, renders the interpretation of results difficult when they concern the evolution of gases through a liquid. But air bubbled through water carries with it a negative charge, and when, as in this case, the emerging gas is both negatively and positively electrified it may be assumed that the electrification is due to the fermentation and not merely to the bubbling.

The author (3) has already demonstrated that electrical effects accompany the decomposition of organic compounds, and as the CO₂ escaping from a fermenting saccharine solution also shows the presence of both positive and negative ions, it may be inferred that the gases liberated during the process of putrefaction are also ionised. This possibility introduces another element for consideration in connection with the researches on the radioactivity of water and soils.

Many investigations have been made upon the presence of radium · emanation in various waters and in the soil air, the detection of the radium emanation being determined by the electroscope and electrometer, and a comparison of the results of these researches with those which are now described offers an interesting parallel. Sir J. J. Thomson (9) has shown that air when bubbled through Cambridge tap water "shows all the peculiarities of a gas in which continuous ionisation is taking place." He also considers that if the effects produced are due to the deposition of a radioactive substance, such substance must have come from the water. Yet upon evaporating the water to dryness upon a metal plate this did not show any ionising power. Adams (10) has followed up the results of Sir J. J. Thomson by an investigation into the nature and properties of this radioactive gas. When comparing it with air blown through distilled water in which a radium compound was dissolved, he found that while these two gases possessed many similarities there were important differences. instance, the solution containing the radium salt, when thoroughly boiled and all the emanation expelled, does not recover its radioactive properties even after a long time, whereas the radioactivity of tap water cannot be entirely destroyed by boiling, and on allowing it to stand it becomes again radioactive, though not to the same extent as before. He also showed that the residue obtained from evaporating large quantities of tap water is not radioactive. Adams considers that these results can only be explained by assuming a continuous production of a radioactive emanation in the water.

These observations of Thomson and Adams appear to lend considerable support to the suggestion that much of the radium emanation found in various waters may be really due to ionised gases formed during the natural decomposition of organic matter through the action of micro-organisms. In such a case "continuous ionisation" would be a natural result, but the residue, after evaporation to dryness, would not be likely to yield any ionising power, as it would not provide suitable conditions for bacterial life.

It may be pointed out that in the account of these experiments there is no mention of their being carried out in such a manner as to exclude bacterial contamination. Boiling would kill all the micro-organisms actively living in the water, but not necessarily those in the spore stage, some of which would probably survive and germinate when the conditions once more became favourable. In certain special cases boiling is even of positive advantage. Miquel (11) has shown that during the process of boiling certain toxins inimical to bacterial life are destroyed, and this is further supported by the experiments carried out by the Massachusetts State Board of Health (12), which show that the power of multiplication of certain bacteria is increased enormously in water which has been boiled.

While it is also thoroughly established by the experiments of Meade Bolton and others (13) that certain water bacteria possess the remarkable power of extensive multiplication in sterilised distilled water, these special forms might not be present; and further, in the absence of organic constituents, one may presume that no ionisation would take place. Thus it is possible to account for the fact that Adams found radioactivity regenerated in tap water but not in boiled distilled water. Unless special precautions were taken it is almost certain that tap water would contain many active bacteria after standing for some time, especially as this contains a small amount of organic matter.

In this connection it is of interest to note that Satterly (14) has found that Cam water taken at Sheep's Green, which would presumably contain more organic matter than Cambridge tap water, also contains twice as much radium.

Joly (15) found a greater amount of radium at Valencia Harbour and at certain localities round the Irish coast than in the open ocean some miles from land. He also found that a part of the radium may be filtered from sea water which contains much organic matter and has been left standing for some weeks, and suggests that it is possibly precipitated by bacterial action in the decomposing organic particles.

Satterly (16) has found that marsh gas (CH₄) collected in the Cam and ditches around Cambridge is radioactive. It is significant that marsh gas is one of the products arising from the decomposition of vegetable matter through the action of bacteria.

The question of atmospheric ionisation has also been the subject of many investigations, since Elster and Geitel demonstrated the presence of radioactivity and ionisation in the atmosphere, and the source of this ionisation has been much studied. These authors, and later Satterly (17), have shown that air sucked up from the earth is ionised, and it is generally admitted that the ionisation of the air is due to ionised gases escaping from the soil or from water.

The influence of meteorological conditions upon the amount of atmospheric ionisation does not at present seem to be very conclusively established. Satterly (18) failed to demonstrate any definite connection between the variations of the barometer and the variations of the ionisation, though some of his observations point to the fact that the ionisation increases with a falling barometer unless accompanied by wet weather. On the other hand, Eve (19) has shown that the emanations increase in amount during cyclones accompanied by heavy rain or rapid thaw and decrease during anticyclones with dry weather and, in winter, low temperatures. He explains that diminishing pressure causes radium emanation, together with other gases, to escape from the ground, and that the moistening of the soil through rain and melting snow promotes the liberation of these gases. On this point it may be noted that, when estimating the bacteria in the Rivers Thames and Lea. Frankland (20) found that during rainy weather the number of bacteria increased enormously as a consequence of the washing of organic matter from cultivated land into the rivers, and hence these micro-organisms were much more numerous during the rainy winter months than in those of the dry summer. Parallel results have been obtained from similar investigations of other rivers. It is also to be observed that the conditions of sudden warmer temperatures with heavy rainfall noted by Eve for the promotion of radium emanation in the atmosphere are also those which favourably influence the activity of bacterial life.

Here again it seems a reasonable hypothesis that part at least of the atmospheric ionisation may be due to ionised gases escaping from the putrefying organic matter present in the soil and water. It has been recognised that the radium emanation by no means accounts for the whole production of ions in the air, and Satterly's (18) experiments bring him to the conclusion that "only a small proportion of the natural ionisation of the air is due to the presence of radium emanation and its products."

Reference may here be made to a former paper (3), in which it was shown that in the case of fermenting glucose separated by a membrane from non-fermenting glucose, the former was negative (zincative) with respect to the latter and also that this proposition was true with regard to putrefying organic matter. From this it may reasonably be inferred that decaying organic matter may have an influence upon the electric potential of the earth's surface, at least in its immediate vicinity.

Though it has not been possible so far to determine quantitatively the ionisation derivable from the activity of the yeast cells nor to give any indication of the relative importance of the processes of ionisation passed in review, yet sufficient evidence has been adduced to establish the fact that fermentation gives rise to ionised gases. Many observations also seem to support the conclusion that some of the ionisation effects noted in the air and in the gases derived from water and the soil may be traced to the natural decomposition of organic matter. I venture, therefore, to set forth a plea that biologic forces should be taken into consideration in seeking the sources of natural ionisation. Nothing is yet known of the possible electrification of the air through the metabolic and physiological activities in plants, and the putrefactive processes alone throughout the whole realm of nature may represent a potent factor in the production of ions and play a part in the cloud and mist formations and other manifestations included in the phenomena of electrification.

The occupation of Armstrong College by the military and its conversion into the Northern Base Hospital in August, 1914, put an end to any further research in my laboratory, and I regret that there has been no opportunity to complete some other work which I had intended to carry out, and many problems connected with this investigation must await further elucidation.

Summary.

The CO₂ liberated during fermentation of glucose through the action of yeast carries both positive and negative ions, and the suggestion is offered that the gases set free during the putrefaction of organic matter are also ionised.

Part of the ionisation of the atmosphere may be attributed to the presence of such ionised gases escaping from the soil and water, and it may be assumed that putrefactive processes in nature exercise an important influence upon various electrical phenomena.

LITERATURE.

- Adams (10). "Water Radioactivity," 'Phil. Mag.,' 1903.
- Brown, Adrian (4). "Influence of Oxygen and Concentration on Alcoholic Fermentation," 'Journ. Chem. Soc.,' 1892.
- Enright (I). "On Electrifications due to the Contact of Gases with Liquids," 'Phil. Mag.,' 1890.
- Eve (19). "On the Amount of Radium Emanation in the Atmosphere near the Earth's Surface," 'Phil. Mag.,' 1908.
- Frankland (20). 'Micro-organisms in Water,' 1894.
- Joly (15). "Radioactivity of Sea Water," 'Phil. Mag.,' vol. 15 (1908).
- Kelvin (7). "Electrification of Air and other Gases by Bubbling through Water and other Liquids," 'Roy. Soc. Proc.,' vol. 57 (1895).
- Massachusetts (12). See Frankland, 'Micro-organisms in Water,' p. 229.
- Meade Bolton (13). See Frankland, 'Micro-organisms in Water,' p. 231.
- Miquel (11). See Frankland, 'Micro-organisms in Water,' p. 228.
- O'Sullivan (5). "On the Rate of Alcoholic Fermentation," Journ. Soc. Chem. Ind., 1898.
- Potter (3). "Electric Effects accompanying the Decomposition of Organic Compounds," 'Roy. Soc. Proc.,' B, vol. 84 (1911).
- Satterley (14). "Note on the Radium-content of the Waters of the Cam, Cambridge Tap Water, and some Varieties of Charcoal," 'Camb. Phil. Soc. Proc.,' vol. 15 (1910).
- --- (16). "The Radioactivity of Marsh Gas," 'Camb. Phil. Soc. Proc.,' vol. 16 (1911).
- (17). "A Study of the Radium Emanation contained in the Air of Various Soils," 'Camb. Phil. Soc. Proc.,' vol. 16 (1911).
- (18). "The Amount of Radium Emanation in the Atmosphere," 'Phil. Mag.,' 1908.
- Slator (6). "Studies in Fermentation. I.—The Chemical Dynamics of Alcoholic Fermentation by Yeast." 'Journ. Chem. Soc.,' 1906.
- Thomson (8). 'Conductivity of Electricity through Gases,' 1906.
- (9). "Experiments on Induced Radioactivity in Air, and on the Electrical Conductivity produced in Gases when they Pass through Water," 'Phil. Mag.,' 1902.
- Townsend (2). "Electrical Properties of Newly Prepared Gases," 'Camb. Phil. Soc. Proc.,' vol. 9 (1898).

The Effect of Temperature on the Hissing of Water when Flowing through a Constricted Tube.

By Sidney Skinner, M.A., and F. Entwistle, B.Sc.

(Communicated by Dr. W. N. Shaw, F.R.S. Received May 20, 1915.)

The tensile strength of liquids has been the subject of study under two different conditions, the first of which may be called the statical condition, and was used by Berthelot* and Worthington,† and more recently by H. H. Dixon. In this method some liquid, at rest in regard to the walls of the containing vessel, is submitted to a stretching force. The second condition, in which the liquid is moving in relation to the walls of the vessel, and is at the same time submitted to a stretching force, has not been studied in detail. Osborne Reynolds has given a general description of the phenomenon, which is of common occurrence. When a liquid is flowing through a pipe of varying section, at the constriction the velocity may be so high that the corresponding diminished pressure in the liquid is This was the subject of his paper read before the sufficient to break it. British Association at Oxford, 1894. He regarded the effect as a boiling of the liquid under diminished pressure, just as boiling may be produced in warm water by removing the surface pressure. The experiments about to be described suggest that the phenomenon in the constricted tube is a true tensile rupture produced in the moving liquid.

Osborne Reynolds describes his experiment thus: "Take a glass tube, say, $\frac{1}{2}$ inch internal diameter and 6 inches long, and draw it down in the middle so as to form a restriction with easy gradual curves so that the inside diameter in the middle is something less than 1/10 inch, leaving the parallel ends of the tube something like $2\frac{1}{2}$ inches each. And then connect one of these parallel ends by flexible hose to a water main which is controlled by a tap. Then, on first opening the tap, the water entering from the main will fill the tube as far as the restriction, and pass through the restriction, but it will not, in the first instance, of necessity fill the tube on the far side of the restriction. If the water is turned on very slowly and the open end of the tube is inclined upwards, then the water will accumulate and fill the tube, displacing the air. But if the water is turned on sharply so that when it reaches the neck it has a velocity of 40 or 50 feet a second, the

^{*} Berthelot, M., 'Ann. de Phys. et de Chim.' (1850).

[†] Worthington, A. M., 'Trans. Roy. Soc.,' London (1892).

[†] Dixon, H. H., 'Transpiration and the Ascent of Sap in Plants' (1914).

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water after passing the minimum section will preserve its velocity and shoot out as a jet from a squirt, not touching the sides of the glass, while if the open end of the tube be held downwards the water, whatever the velocity, will, after passing the restriction, run out of the tube without filling it.

"In neither of these cases is there any hiss or sound except such as is caused by the free jet passing through the air.

"But on holding the open end of the tube upwards and quietly filling both limbs of the tube by opening the tap very quietly, and then turning on more water, the water will not shoot out in a jet but will come out like any other stream—as it might do if there were no restriction.

"At first, while the velocity through the neck is below 50 feet per second, there is no sound, but as soon as a velocity of 54 feet per second is attained, or a little more, a distinct sharp hiss is heard—exactly resembling that of the kettle or the hiss of the water through a tap."

If this phenomenon was the simple boiling of the water it is evident that, if the water were raised to 100° C, and then passed through such a tube the hissing would occur with practically no velocity. This critical point of hissing has been studied with water and with certain other liquids. The first experiments were with tap water.

In order to have a large supply of hot water to force through a constricted tube a 2-gallon can was taken and a tubulure was fixed in the base which could be connected with the high-pressure water supply, and a second tubulure was attached near the top of the can, to which could be attached a constricted glass tube, the ordinary mouth of the can being closed with a wired-on cork, carrying a brass stopcock. The high-pressure water supply was fed by a cistern about 70 feet above the level of the apparatus, so that the pressure could be of any value up to 70 feet of water. The constricted glass tube was bound on to the upper tubulure of the can by means of a rubber and wire. The can was placed on a tripod and could be heated from below. The investigation of the velocity required to give the hiss was made by raising the water in the can to the required temperature, closing the tap at the top of the can, and then forcing that bulk of warm water through the constriction by turning on the tap connected to the high-pressure supply. When the pressure had been adjusted so as just to get the hiss at the constriction the velocity of the stream was measured by collecting the water which flowed out in a given time. The temperature of the water was obtained either by plunging a thermometer into the collected water, or by arranging the thermometer in the escape tube so that the temperature of the escaping stream was observed. The results, which are given in the following Table,

Decembe	December 5, 1918.	December	December 12, 1913.	Бесешье	December 17, 1913.	December 19, 1913.	19, 1913.	July 17, 1914.	, 1914.
Temperature of escaping water.	Mass collected in 40 seconds.	Temperature of escaping water.	Mass collected in 40 seconds.	Temperature of escaping water.	Mass collected in 40 seconds.	Temperature of escaping water.	Mass collected in 40 seconds.	Temperature of escaping water.	Mass collected in 40 seconds.
° C.	grm. 759	° C. 13·0	grm. 1092	° C. 13·2	grm. 1120	° C. 11.7	grm. 1060	° C. 19·3	grm. 1099
9-61	762	25 -3	1067	30 is	1045	31.0	1145	\$3 \$8 \$7	1044
32 .5	748	38.5	1034	40 °5	1067	47.5	6201	45 û	866
4 0 0	069	2.0.5	7 86	48.3	1036	0. 29	1020	47.2	972
£6 -3	723	9.02	096	45.0	1001	72.0	946	24.7	1017
55 .5	7117	0.42	838	23.0	970	82.7	787	6. 49	941
58.4	737	88 5	884	71.0	744	0.96	792	Ç 98	80%
8.09	199	· · · · · · · · · · · · · · · · · · ·		81 .5	803			0-66	833
0.11	989								
2.11	4								
When M = 0. T =	0, T = 356°.	When M = 0, T = 363°.), T = 363°.	When $M = 0$. $T = 279^2$.	$T = 279^{\circ}$.	When $M = 0$. $T = 293$.). T = 293°.	When M = 0. T = 350°). T = 350°.

were plotted in diagrams which showed the mass of water passing in a fixed time against the temperature; when these points were examined it was found that they could be represented in general by straight lines.

These straight lines when prolonged cut the axis of temperature at a point which, if the mean of the above observations to be taken, is 328° C., or, in other words, they appear to cut the temperature axis at a temperature which is approaching the critical point of water, 365°. In this they resemble the temperature coefficient of surface tension. This result at once indicates that, in the case of water, the phenomenon of the hiss would apparently cease near the critical temperature of the water—a result which might be expected if the view is taken that the critical temperature is the temperature at which the tensile strength is zero. It certainly is against the view, which was put forward by Osborne Reynolds, that the phenomenon is ordinary boiling.

When a calculation is made to find the critical velocities of flow, using the formula $V_c = 1000\eta/\rho r$ where η is the viscosity, ρ the density, and r the radius of the constriction at the smallest section, 0.076 cm. in the case of the tube used in many of these experiments, it appears that the observed velocity in these experiments is always greater by far than the critical velocity. This result would show that the flow is not the orderly flow of stream-line motion, although on the inflowing side of the constriction owing to the trumpet shape of the constriction it may be flow of this character, and the turbulent portion may be confined to the outflowing portion of the stream. These considerations have led us to be cautious in applying Bernouilli's formula, by which the fall of pressure at the constriction might have been calculated. If this had been justifiable an estimate might have been obtained of the actual negative pressure to which the water was exposed.

When the experiment is working properly the bubbles formed at the constriction are extremely small, and give the stream a cloudy appearance. When the temperature of the water is high, nearing that of the ordinary boiling point, on some occasions large bubbles were formed, breaking up the hot stream. These bubbles were like those of ordinary boiling, and it is probable were formed when the stream coming from the hot tank where the water was under pressure bursts into boiling, somewhat after the manner of a geyser. The water may have been superheated to a slight degree when this was observed. If it had been possible to maintain in the apparatus some slight back pressure this might have been prevented; but it was not possible with the apparatus at command.

The conclusions to which the experiments lead are:

1. That the phenomenon of hissing of water passing a constriction is due to a true rupture of the stream at the point where the pressure is lowest.

2. That the temperatures at which the hissing just occurs, between 0° and 100° C., follow a law which may be expressed

$$V = C(\theta - t)$$

where V is the velocity of the stream at a temperature t, θ the critical temperature of water, and C a constant.

Experiments are being continued with other liquids, but the form of apparatus has to be modified with them, and we are not yet satisfied that the new form reproduces the required conditions.

Ionisation Potentials of Mercury, Cadmium, and Zinc, and the Single- and Many-lined Spectra of these Elements.

By J. C. McLennan, F.R.S., and J. P. Henderson, University of Toronto.

(Received May 28, 1915.)

[PLATE 6.]

I. Introduction.

In a paper by Frank and Hertz in the 'Physikalische Zeitschrift,'* these investigators have shown that the minimum energy required to ionise an atom of mercury is that acquired by an electron in passing through a fall of potential of 4.9 volts. These writers have also shown in a later communication† that when heated mercury vapour is traversed by electrons possessing energy slightly above this amount the vapour is stimulated to the emission of the single spectral line $\lambda = 2536.72$ Å.U. This result constitutes a new and most interesting application of the quantum theory, for it will be seen that in the relation $Ve = h\nu$, where $h = 6.6 \times 10^{-27}$ erg sec., 4.9 volts is the potential fall which corresponds to the frequency ν of the line $\lambda = 2536.72$ Å.U. If the relation just pointed out be applicable generally to all the elements it follows that if the vapour of an element can be shown to be capable of exhibiting a single-line spectrum, the frequency of this single spectral line may be used to deduce the minimum amount of energy required to ionise the atoms of that element.

With the object of establishing such a generalisation, if possible, some experiments were recently made by the writers, and it has been found that

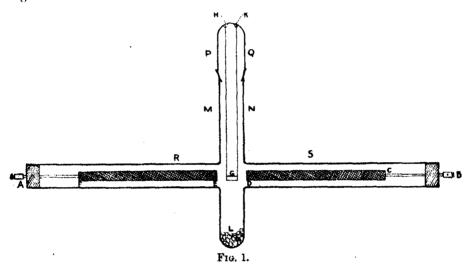
^{* &#}x27;Verh. d. D. Phys. Ges.,' vol. 10, pp. 457-467.

^{† &#}x27;Verh. d. D. Phys. Ges.,' vol. 11, p. 512.

the vapours of cadmium and zinc as well as that of mercury can be stimulated to the emission of single-line spectra when traversed by electrons possessing the requisite amount of energy. With cadmium vapour the wave-length of the line constituting this single-line spectrum is $\lambda = 3260 \cdot 17$ Å.U., while that of the single-line spectrum of zinc vapour is $\lambda = 3075 \cdot 99$ Å.U. By the quantum theory it follows then that the minimum ionising potentials for cadmium and zinc vapours are respectively 3.74 volts and 3.96 volts.

II. Apparatus.

In carrying out the experiments the form of arc used is that shown in fig. 1.



The apparatus consisted of a tube of fused quartz possessing three arms R, S, and MN, and a receptacle L. Some of the metal to be used in the arc was placed in the receptacle L, and two rods of the same metal FE and DC were attached to two wires and these latter were in turn fastened to two brass plugs, A and B, which were sealed into the tubes R and S with mastic wax. A small piece of sheet platinum was attached to two wires which constituted the heating circuit and these were sealed with platinum wire into a glass tube PQ at H and K. The open end of the glass tube PQ was ground so as to fit exactly into the end of the quartz tube MN as shown in the diagram. The arms MN, R, and S were each about 40 cm. long, and it was found with this length that when the receptacle L was strongly heated with a Bunsen burner the wax joints at A and B and the ground one at the end of the tube MN remained quite cool.

In the experiments the plate G was coated with a thin layer of either calcium oxide or barium oxide. When the tube was in operation the terminals of an auxiliary heating circuit were attached at H and K, B and K were joined by a wire and the arcing voltage was applied between B and A, the latter being the positive terminal. With this arrangement G and D constituted a double cathode. The tube was highly exhausted with a Gaede mercury pump through a glass tube which was sealed into an opening in the brass end-piece at A.

In taking photographs the plate G was brought to incandescence by means of the auxiliary heating current, the metal in L was strongly heated with the flame of a Bunsen burner so as to keep the plate G surrounded with the vapour of the metal, and the collimator of a small spectrograph with a quartz train was directed at the incandescent plate G. A short tube of asbestos was attached to the quartz tube directly in front of this plate, so that the radiation from the arc passed through it to the slit of the spectroscope. This arrangement was found necessary in order to cut off the radiation from the Bunsen flame itself. It should be noted that in studying the radiation from mercury vapour the electrodes CD and FE were simply stout iron wires.

III. Characteristics of Arcs of the Different Metals.

With the arrangement just described it was found that when the direct current 110-volt circuit, with suitable resistances in series, was applied to the terminals A and B, and the plate G brought to incandescence, strong arcs could be maintained for hours with all three metals. With the 220-volt circuit applied the arcs of all three metals could be made most intense, and could also be maintained for long periods. With the 220-volt circuit it was found that, when the arc was once struck, it could be easily maintained for a considerable time without the continued use of the oxy-cathode G. With low voltages, however, it was always necessary to maintain the plate G at incandescence in order to keep the arc established.

In commencing the investigation efforts were first directed to ascertaining the minimum voltages which should be applied between G and E in order to produce what may be called the many-lined spectrum of the different metals. These spectra are shown in the upper parts of figs. 2, 3, and 4. With mercury a difference of potential 12.5 volts was found to be necessary, with zinc 11.85 volts, and with cadmium 15.3 volts. With differences of potential below these respective values, but above 3 volts, it was found that the only spectrum which could be obtained for each of the metals was one which contained but a single line. Illustrations of these single-line spectra are shown in the lower portions of figs. 2, 3, and 4.

That for mercury, and shown in fig. 2, $\lambda = 2536.72$, was obtained with an areing potential difference of 9 volts, with an exposure of two hours and a-half. This single-line spectrum was also obtained with a potential fall of 5 volts, but it was only just visible on the plate with a five-hour exposure. With 3 volts and a five-hour exposure the line was not obtained. The continuous white band shown on the left of the spectrogram was due to the incandescent platinum. The line $\lambda = 3075.99$ Å.U., shown in the lower spectrogram of fig. 3, was obtained with zine vapour, with an arcing potential of 10.5 volts, with an exposure of three hours. According to the quantum theory relation, $Ve = h\nu$, this line should have been obtained with any potential difference above 3.96 volts, but no attempt was made with this element to ascertain with any exactness the least potential difference with which the line could be brought out.

The line $\lambda=3260\cdot17$ Å.U., shown in the lower spectrogram of fig. 4, was obtained with cadmium vapour, with an arcing potential difference of 13.6 volts. With an arcing potential of 3.4 volts and a three-hour exposure no trace of the line was obtained with this element. With this metal, as with zinc, no special effort was made to determine with any exactness the least potential difference which would bring out the line.

IV. Discussion of Results.

The investigation thus far has shown that it is possible to obtain spectra, each consisting of a single spectral line, with mercury, zinc, and cadmium vapours. To obtain these single-line spectra arcing potentials must be used which are lower than 12.5 volts, 11.85 volts, and 15.3 volts, which values have been found to be the minimum potential differences required to bring out the many-lined spectra for mercury, zinc, and cadmium respectively. From the work done with mercury, it would appear that the range of voltages which will bring out a single-line spectrum for an element is a very definite one, and extends from the potential difference corresponding to the frequency of the line given by the quantum theory to the potential difference which brings out the many-lined spectrum.

A point which should be mentioned in connection with this work is that, to bring out these single-line spectra, it was found that the best results could be obtained only when suitable vapour densities were used. The light corresponding to the lines in the single-line spectra of the three elements is known to be strongly absorbed by the respective vapours, and, if vapours of too great density be used, then the lines do not come out on the plates on account of absorption. On the other hand, if the vapours be too

Fig. 2.

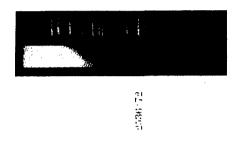


Fig. 3.

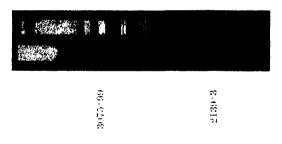
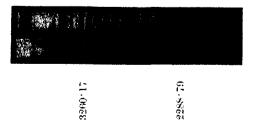


Fig. 4.



rare, the intensity of the light is so weak that photographic traces of the lines cannot be obtained without extremely long exposures.

In attempting to offer an interpretation of the following facts: (1) that single-line spectra can be obtained with mercury, zinc, and cadmium vapours with a definite range of arcing voltages, (2) that the many-lined spectra for these elements are also obtainable with definite minimum arcing potential differences, and (3) that the conditions for obtaining these two classes of spectra are sharply differentiated, one cannot as yet speak with certainty. It will be recalled, however, that Sir J. J. Thomson,* in his work with positive rays, found that it was possible to ionise an atom of mercury in two, and only two, definite ways, that is, by removing either one electron from the atom or by removing eight of them. An obvious interpretation of his discovery would be that if an atom consists of a positive nucleus with one or more rings of electrons revolving about it, then the mercury atom may be supposed to have eight electrons in its outer ring, and that ionisation consists either in the removal of one electron from the atomic system or else in the removal of the whole eight electrons which constitute the outer ring. This may be taken to indicate that one can remove one electron, but only one, from the outer ring without completely destroying its stability. This explanation would fit in with the results described in the present paper, and it would seem, therefore, that the energy required to remove an electron from mercury, zinc, and cadmium atoms is that possessed by an electron which has passed through a fall of potential of 4.9 volts, 3.96 volts, and 3.74 volts respectively. To remove the outer ring of electrons from the atoms of these three elements the energy necessary would be that acquired by an electron under potential differences of 12.5 volts, 11.85 volts, and 15.3 volts respectively. The single-line spectra could then be explained by supposing that they had their origin in the recombination of the singly ejected electrons with the parent atoms, and on this view the explanation of the production of the many-lined spectra referred to above would be that they have their origin in the radiations emitted in the re-establishment of the complete outer ring of electrons in the atoms from which they had been removed.

In considering the probable range of wave-lengths covered by the many-lined spectra of the three elements, it may be pointed out that if the quantum theory be applicable the relation $Vc = h\nu$, combined with the minimum voltages which produce the spectra, enables one to calculate their upper limiting frequencies.

^{*} Sir J. J. Thomson, 'Rays of Positive Electricity and their Application to Chemical Analysis,' p. 49.

With the values 12.5 volts, 11.85 volts, and 15.3 volts, it follows that the shortest wave-length in the many-lined spectrum of mercury should be given by $\lambda = 975.3$ Å.U., while that in the spectrum of zinc should be given by $\lambda = 1281.8$ Å.U., and that in the cadmium spectrum by $\lambda = 797$ Å.U.

It was pointed out by Paschen* in 1909 that the emission spectra of mercury, zinc, and cadmium should include a series of single lines represented by $\nu=1.5$, S-m, P. The limiting wave-lengths for these series are for mercury $\lambda=1188$ Å.U., for zinc $\lambda=1320$ Å.U., and for cadmium $\lambda=1378.7$ Å.U., which values it will be seen approximate to those calculated by the application of the quantum theory. The actual existence of the series lines represented by $\nu=1.5$, S-m, P, was demonstrated by Wolff* some two years ago, and members of the series were picked out by him as far down as $\lambda=1402.72$ Å.U. for mercury, $\lambda=1376.87$ Å.U. for zinc, and $\lambda=1423.23$ Å.U. for cadmium.

At present there appears to be no evidence of the existence of lines in the arc spectra of these three elements of wave-length shorter than those given by the relation $\nu=1.5$, S-m, P, so that it may very well be that the limiting lines of these series represent the limiting ones of the spectra arising from disturbances set up in the outer ring of electrons in the atoms of mercury, zinc, and cadmium.

The arcing voltages used by Wolff were higher than the lowest ones found by the writers in the present investigation to be capable of producing the many-lined spectra, but in all probability such higher voltages, while adding to the intensities of the lines obtained, would not add anything to the possible number of lines obtainable, unless these voltages were sufficiently great to produce disturbances in rings of electrons closer in to the nuclei of the atoms than the outermost ones. That disturbances in the inner rings of electrons are possible seems to be proven by the existence of Röntgen ray and γ -ray spectra. It would have been interesting to see if the series of lines $\nu = 1.5$, S-m, P, predicted by Paschen and discovered by Wolff, were obtainable with voltages so low as those used in the present investigation, but, owing to the lack of a vacuum grating spectroscope, experiments to investigate this point could not be carried out by the writers.

It should be pointed out that the lines $\lambda = 2536.72$ Å.U., $\lambda = 3075.99$ Å.U. and $\lambda = 3260.17$ Å.U. are respectively the first members of Paschen's‡ combination series $\nu = 2$, $p_2 - m$, S for the elements mercury, zinc, and cadmum.

^{*} Paschen, 'Ann. der Phys.,' vol. 30, p. 746 (1909), and vol. 35, p. 860 (1911).

[†] Wolff, 'Ann. der Phys.,' vol. 42, p. 825 (1913).

[!] Paschen, loc. cit.

V. Summary of Results.

- 1. It has been shown that a spectrum consisting of a single line is obtainable for mercury, for zinc, and for cadmium.
- 2. The wave-lengths of these lines are for mercury $\lambda = 2536.72$ Å.U., for zine $\lambda = 3075.99$ Å.U., and for cadmium $\lambda = 3260.17$ Å.U.
- 3. The minimum ionisation potentials for mercury, zinc, and cadmium have been shown to be 4.9 volts, 3.74 volts, and 3.96 volts respectively.
- 4. Some considerations have been presented which support Sir J. J. Thomson's theory of the two type ionisation of atoms of mercury, and others which suggest that the theory is applicable as well to the ionisation of atoms of zinc and cadmium.
- 5. The minimum arcing potential differences which will bring out the many-lined spectra of mercury, zinc, and cadmium vapours were found to be 12.5 volts, 11.8 volts, and 15.3 volts respectively. These voltages are also probably the minimum ionisation potentials of the second type for the atoms of these three elements.
- 6. Considerations have been presented which suggest the possibility of analysing the spectrum of an element in such a way as to enable one to correlate different portions of the spectrum with disturbances in definite portions of the atomic structure of that element.

The writers, in conclusion, wish to acknowledge their indebtedness to Mr. P. Blackman for assistance in taking the photographs and to Mr. F. Mezen for his help in blowing the quartz tubes.

On the Partial Correlation Ratio. By Karl Prasson, F.R.S.

(Received May 31, 1915.)

- (1) In a paper communicated to the Royal Society in 1903* I gave very briefly in a footnote the properties of the correlation ratio. These properties were discussed more at length in my memoir, "On the General Theory of Skew Correlation and Non-linear Regression," published in 1905. two papers dealt only with the total correlation ratio, or the relation between two variates without consideration of any other correlated variates. The introduction of the correlation ratio enabled the measure of the relationship between two variates to be expressed by a single number, measuring its total intensity, in cases where the regression line was of any form. The ratio passed into the usual correlation coefficient when the regression line became straight. This correlation ratio has been generally accepted by statisticians as a useful measure of relationship in cases of skew correlation and non-linear regression. Shortly after the appearance of the above memoirs I generalised this coefficient in a manner comparable with the generalisation of the coefficient of correlation, namely, by the definitions of the multiple correlation ratio and of the partial correlation ratio. ratios correspond to the multiple correlation coefficient and the partial correlation coefficient in multiple linear regression. Their importance is very considerable, as they enable us to measure the intensity of association between two variates when other correlated variates are considered as constant without any assumption that the regression is linear, still less that the frequencies follow the normal (or Laplace-Gaussian) surface. I had not intended to discuss the results of the present paper before the probable errors had been provided, but the recent revival of interest in skew regression, and its fundamental importance in all higher statistical inquiry, justifies, at least, the publication of those formulæ which are fundamental to the subject.
- (2) I deal first with the problem of three variates, although the extension to any number is not hard to make.

Let these three variates be x, y, and z; further, let the symbol ${}_{x}\eta_{y,x}$ signify the partial correlation ratio of y on x for a constant z. Similarly, ${}_{x}\eta_{x,y}$ signifies the partial correlation ratio of x on y for a constant z.

^{* &#}x27;Roy. Soc. Proc.,' vol. 71, pp. 303-4.

^{+ &}quot;Mathematical Contributions to the Theory of Evolution," XIV, 'Drapers' Company Research Memoirs' (Cambridge University Press).

If we take for a given value of z, say z_p , the corresponding x, y population we can determine in the usual manner the special correlation ratio of y on x for this selected population. It may be represented by $z_p\eta_{y,x}$; then by definition of a correlation ratio:—

$$(1-_{z}\eta^{2}_{y,z}) = \frac{S_{z}S_{y}\left\{_{z_{\rho}}n_{xy}(y-_{z_{\rho}}\bar{y}_{z})^{2}\right\}}{_{z_{\rho}}n_{z_{\rho}}\sigma^{2}_{y}}.$$

Here the subscript z_p affixed means limitation to the population of x and y selected by giving z the constant value z_p . Thus $z_p n$ is the whole frequency of such a population, $z_p \bar{y}_x$ the mean value for such a population of the array of y's corresponding to a given x, $z_p \sigma_y$ the standard deviation of all y's in such a population. The summations S_x , S_y are also to be for this limited field, while $z_p n_{xy}$ is any cell frequency x, y in the same field.

I now define my partial correlation coefficient $z\eta_{y,x}$ by stating that $(1-z\eta_{y,x}^2)$ × mean value of $z_{\rho}\sigma_y^2$ shall be taken as the weighted mean of such expressions as $(1-z_{\rho}\eta_{y,x}^2)$ × $z_{\rho}\sigma_y^2$ for all values of z. But the mean value of $z_{\rho}\sigma_y^2 = \sigma_y^2(1-\eta_{y,x}^2)$ by definition. Hence,

$$(1 - {}_{z}\eta^{2}{}_{y,z})(1 - \eta^{2}{}_{y,z})\sigma_{y}^{2} = S_{z} \left\{ {}_{z_{p}}n \left(1 - {}_{z_{p}}\eta^{2}{}_{y,z}\right) {}_{z_{p}}\sigma_{y}^{2} \right\} / N,$$

if N be the total population,

=
$$S_x S_x S_y \{ z_{\mu} n_{xy} (y - z_{\mu} \bar{y}_x)^2 \} / N$$
.

Now $z_{j}\bar{y}_{x}$ is clearly the mean value of y for the group of y's corresponding to a constant z and x, and may be written \bar{y}_{zx} ; we may accordingly read our triple summation as

$$S_{z}S_{x}S_{y} \left\{ n_{xyz} (y - \bar{y} + \bar{y} - \bar{y}_{xz})^{2} \right\} / N = S_{z}S_{x}S_{y} \left\{ n_{xyz} (y - \bar{y})^{2} \right\} / N + S_{z}S_{z}S_{y} \left\{ n_{xyz} (\bar{y} - \bar{y}_{xz})^{2} \right\} / N + 2S_{z}S_{x}S_{y} \left\{ n_{xyz} (y - \bar{y}) (\bar{y} - \bar{y}_{xz}) \right\} / N.$$

The first of these sums is clearly σ_y^2 . In the third of these sums the factor changing with y is $n_{zyz}(y-\bar{y})$, and summed for y this equals

$$S_{y}\left\{n_{xyz}(y-\bar{y})\right\} = n_{xz}(\bar{y}_{xz}-\bar{y}).$$

Hence the third sum equals

$$-2 S_x S_x \{n_{xx} (\bar{y} - \bar{y}_{xz})^2\} / N$$

which is precisely double the second sum after summing for y. Thus our triple summation

$$= \sigma_y^2 - S_z S_z \left\{ n_{zz} (\bar{y} - \bar{y}_{zz})^2 \right\} / N.$$

I write the last summation

$$\mathbf{H}^{2}_{y\cdot xs}\sigma_{y}^{2}$$
.

 $\mathbf{H}_{y,x}$ is comparable with $\eta_{y,x}$; it is the correlation ratio—not of y on

arrays of x, but of y on arrays of x with z. It must be carefully distinguished from $n_{y,x}$, which is a true partial correlation ratio. We have,

$$(1 - z\eta_{y,z}^{2})(1 - \eta_{y,z}^{2}) \sigma_{y}^{2} = \sigma_{y}^{2} - H_{y,zz}^{2} \sigma_{y}^{2},$$

$$z\eta_{y,z}^{2} = \frac{H_{y,zz}^{2} - \eta_{y,z}^{2}}{1 - \eta_{y,z}^{2}}.$$

or

To test this result suppose the regressions to become linear, then $\eta_{y,z}$ becomes the correlation coefficient r_{yz} , and $H_{y,zz}$ becomes $R_{y,zz}$, the multiple correlation coefficient between y and x with z, which is well known to be given by

$$R^{3}_{y,zz} = \frac{r^{2}_{yz} + r^{2}_{yz} - 2 \, r_{yz} r_{yz} r_{zz}}{1 - r^{2}_{zz}}.$$
Hence
$$z\eta^{2}_{y,z} = \frac{\frac{r^{2}_{yz} + r^{2}_{yz} - 2 \, r_{yz} r_{yz} r_{zz}}{1 - r^{2}_{zz}} - r^{2}_{yz}}{1 - r^{2}_{yz}}$$

$$= \frac{(r_{yz} - r_{zz} r_{yz})^{2}}{(1 - r^{2}_{yz})(1 - r^{2}_{zz})},$$
or
$$z\eta_{y,z} = \frac{r_{yz} - r_{zz} r_{yz}}{\sqrt{(1 - r^{2}_{yz})(1 - r^{2}_{zz})}},$$

$$= z^{r_{yz}},$$

that is to say the partial correlation ratio becomes in this case, as it should do, the partial correlation coefficient.

 $H_{y,zz}$ is a "multiple correlation ratio," just as $R_{y,zz}$ is a "multiple correlation coefficient." Just as the partial correlation coefficient can always be deduced from the formula

$$zr_{yx} = \sqrt{\frac{R^2_{y \cdot xx} - r^2_{yx}}{1 - r^2_{yx}}},$$

so the "partial correlation ratio" can always be found from

$$_{s}\eta_{y..z} = \sqrt{\frac{H_{y..zz}^{2} - \eta_{y..s}^{2}}{1 - \eta_{y..z}^{2}}}$$
.

In this lies the importance of the determination of the expressions for the value of $H_{\nu,zz}$.

If x and z be given by classes or categories and y be a quantitative variate, then $H_{y,zz}$ can clearly be found from

$${
m H^2}_{y.\,xz} = {{
m S}_z {
m S}_z \left\{ n_{xz} (\bar{y} - \bar{y}_{xz})^2
ight\} \over {
m N} \sigma_y^2} \, ,$$

and $\eta_{y,x}$ will also be ascertainable.

For example, we might ask for the relationship between convictions for

drunkenness per year of adult life and mental capacity for a constant grade of health. The above formula for the partial correlation ratio in terms of the multiple correlation ratio was deduced by me some years ago as suitable for dealing with certain variates in criminology. It is laborious in use, owing to the work needful to evaluate numerically $H_{y.zz}$ when the grouping is at all fine. Quite recently Mr. Isserlis, in a very valuable memoir,* has investigated some of the conditions under which the determination of $H_{y.zz}$ may be thrown back on quantities like $\eta_{z.y}$, $\eta_{z.z}$, $\eta_{y.z}$, $\eta_{z.y}$, r_{xy} , r_{xz} , r_{yz} , etc., which depend solely on paired variates, i.e., on the "marginal total tables" of the "correlation (or contingency) solid." This is an important conception and corresponds to the expression of the multiple correlation coefficients $R_{y.zz}$ in terms of the total coefficients r_{zy} , r_{yz} , r_{zz} .

(3) It is clear that the six partial correlation ratios $_{x}\eta_{y,z}$, $_{x}\eta_{z,y}$, $_{y}\eta_{z,z}$, $_{y}\eta_{z,z}$, $_{z}\eta_{y,z}$, and $_{z}\eta_{x,y}$ are not independent, but connected with each other, pair and pair, and with the three multiple correlation ratios, $H_{y,xz}$, $H_{x,yx}$, $H_{x,zy}$, by the equations,

$$\frac{1 - x\eta^{2}_{y \cdot x}}{1 - \eta^{2}_{y \cdot x}} = \frac{1 - x\eta^{2}_{y \cdot x}}{1 - \eta^{2}_{y \cdot x}} = \frac{1 - H^{2}_{y \cdot xz}}{(1 - \eta^{2}_{y \cdot x})(1 - \eta^{2}_{y \cdot x})},$$

$$\frac{1 - y\eta^{2}_{z \cdot x}}{1 - \eta^{2}_{z \cdot x}} = \frac{1 - x\eta^{2}_{z \cdot y}}{1 - \eta^{2}_{z \cdot y}} = \frac{1 - H^{2}_{z \cdot y}}{(1 - \eta^{2}_{z \cdot x})(1 - \eta^{2}_{z \cdot y})},$$

$$\frac{1 - x\eta^{2}_{x \cdot y}}{1 - \eta^{2}_{x \cdot y}} = \frac{1 - y\eta^{2}_{x \cdot z}}{1 - \eta^{2}_{x \cdot z}} = \frac{1 - H^{2}_{x \cdot xy}}{(1 - \eta^{2}_{x \cdot y})(1 - \eta^{2}_{x \cdot z})}.$$

Thus the labour of calculating the six partial correlation ratios reduces to that of finding the six total η 's and the three H's or multiple correlation ratios.

(4) In the usual notation ${}_{3\cdot4...m}r_{12}$ represents the partial correlation coefficient of the first and second variates for constant 3, 4, ..., m variates, and $R_{1\cdot284...m}$ represents the multiple correlation coefficient of the first variate with regard to the combined 2, 3, 4, ..., m variates. If Δ be the determinant

where $r_{ss'} = r_{s's}$ is the correlation coefficient of the s and s' variates, and Δ_{pq}

^{* &#}x27;Biometrika,' vol. 10, pp. 391-411.

be the minor of the constituent r_{pq} , Δ_{pq} , p'q' the second minor of the constituents r_{pq} and $r_{p'q'}$, then it is well known that*

$$_{34...m^{p_{12}}} = \frac{\Delta_{12}}{\sqrt{(\Delta_{11}\Delta_{22})}},$$

$$1 - R^{2}_{1.234...m} = \frac{\Delta}{\Delta}.$$

and+

Thus we have

$$1 - {}_{34...m}r_{12}{}^{2} = \frac{\Delta_{11}\Delta_{22} - \Delta_{12}{}^{2}}{\Delta_{11}\Delta_{22}}.$$

But by a familiar theorem in determinants

$$\Delta_{1122} = (\Delta_{11}\Delta_{12} - \Delta_{12}^{2})/\Delta,$$
hence
$$1 - \frac{\Delta \cdot \Delta_{1122}}{\Delta_{11}\Delta_{22}} = \frac{\Delta/\Delta_{11}}{\Delta_{22}/\Delta_{2211}},$$

$$= \frac{1 - R^{2}_{1 \cdot 23 \dots m}}{1 - R^{2}_{1 \cdot 3 \cdot m}},$$
or
$$= \frac{1 - R^{2}_{2 \cdot 13 \dots m}}{1 - R^{2}_{2 \cdot 23 \dots m}},$$

or

since the left-hand side is symmetrical in 1 and 2. By successive reduction we can clearly write!

$$1 - {}_{34\dots m}r_{12}{}^{2} = \frac{1 - R^{2}_{1 \cdot 23 \cdot m}}{(1 - {}_{45\dots m}r_{13}{}^{2})(1 - {}_{56\dots m}r_{14}{}^{2})(1 - {}_{67\dots m}r_{15}{}^{2})\dots(1 - r_{1m}{}^{2})},$$

which allows us to express the partial correlation coefficient of the (m-2)th order in terms of the multiple coefficient of correlation of the (m-1)th order, and partial correlation coefficients of the (m-3)th, (m-4)th, (m-5)th, ..., and zero orders.

Now practically identical formulæ hold connecting the partial correlation ratio of the (m-2)th order with multiple correlation ratios, except that 1 and 2 are no longer interchangeable.§ We have, in fact

$$1 - \frac{1}{34...m} \eta^{2}_{1\cdot 2} = \frac{1 - H^{2}_{1\cdot 23...m}}{1 - H^{2}_{1\cdot 24...m}}, \tag{\beta}$$

or by successive reduction we deduce

$$1 - {}_{34\dots m}\eta^2{}_{1\cdot 2} = \frac{1 - H^2{}_{1\cdot 23\dots m}}{(1 - {}_{45\dots m}\eta^2{}_{1\cdot 3})(1 - {}_{56\dots m}\eta^2{}_{1\cdot 4})(1 - {}_{67\dots m}\eta^2{}_{1\cdot 5})\dots(1 - {}_{72\dots m})}. \quad (\gamma)$$

- * 'Phil. Trans.,' A, vol. 200, p. 10 (1902), Eqn. xxvii.
- † 'Biometrika,' vol. 8, p. 439, eqn. vi.
- † This result was first given by Yule, 'Roy, Soc. Proc.,' A, vol. 79, p. 189 (1907), Eqn. (17).
- § In skew regression η_u ., is of course not equal to η_v ., although numerically both lie between $r_{uv} = r_{vu}$ and unity.

Since on the left and in the numerator of the right any of the variates 3, 4, ..., m, are interchangeable without changing the values of the left-hand side or the numerator, it follows that an immense variety of forms can be given to the partial correlation ratios in the denominator. Further, no one of these partial correlation ratios can be perfect, *i.e.* equal unity, without the multiple correlation ratio $H_{1.23...m}$ being also perfect, and this remark applies to every multiple correlation ratio of a higher order, *i.e.* if $s(s+1)...m\eta_{1.(s-1)} = 1$ then will $H_{1...mp+1)...s...m} = 1$, p being > s.

It will be clear that our results (α) for the partial correlation ratios of the first order are only very special cases of (β), or rather (γ), above.

To demonstrate (β) is little more than a matter of the definitions of our high order partial correlation ratio and our multiple correlation ratio.

By definition

$$\mathbf{H}^{2}_{1\cdot 23\dots m} = \frac{\mathbf{S}_{z_{1}}\mathbf{S}_{z_{1}}\dots \mathbf{S}_{z_{m}}\left\{n_{23\dots m}(\bar{x}_{1}-\bar{x}_{1\cdot 234\dots m})^{2}\right\}}{\mathbf{N}\sigma_{z_{n}}^{2}},$$

 $\bar{x_1}$ being the general mean of the first variate and $\bar{x_1}$. 234...m the partial mean for constant 2nd, 3rd, 4th, ..., mth variates, whence we can deduce*

$$1 - \mathrm{H^2_{1.28...m}} = \frac{\mathrm{S_{z_1}S_{z_1...S_{z_m}}} \{ n_{28...m} (x_1 - \bar{x_1} \cdot {}_{23...m})^2 \}}{\mathrm{N}\sigma_z^2},$$

or $\sigma_{x_1}^{\ 2}$ (1 — $H_{1 \cdot 23 \dots m}$) is the mean square standard deviation of arrays of x_1 for constant values of the m-1 other variates x_2, x_3, \dots, x_m . But we have originally defined $\eta_{1 \cdot 2}$ by saying that $\sigma_{1}^{\ 2}$ (1 — $\eta_{1 \cdot 2}^{\ 3}$) shall be the mean square standard deviation of the arrays of the first variate which correspond to constant values of the second variate. Now let these arrays of the first variate be still further limited by being taken for constant values of the 3rd to the mth variates. Then consider the expression:

$$84...m\sigma_1^{9}(1-84...m\eta^{3}_{1.2}),$$

where 24...mo1² is the mean squared standard deviation of the first variate for constant 3rd to the mth variates. This by analogous definition is the mean squared standard deviation of the 1st on the 2nd variate for constant 3rd to the mth variates, i.e., for 1st on 2nd to mth variate.

$$= S_{x_2}S_{x_2}...S_{x_m} \{n_{23...m} (x_1 - \bar{x}_1...s_{3...m})^2\}/N$$

$$= \sigma_1^2 (1 - H^2_{1..23...m}).$$

$$1 - \frac{1}{34...m} \eta_1...s^2 = \frac{\sigma_1^2 (1 - H^2_{1...23...m})}{34...m}.$$

Thus

But clearly $a_{1..m}\sigma_1^2 = \sigma_1^2 (1 - H^2_{1.84..m})$, and there results

$$1 - {}_{84..m}\eta^{2}_{1\cdot 2} = \frac{1 - H^{2}_{1\cdot 324...m}}{1 - H^{2}_{1\cdot 34...m}}.$$
 (3)

* Isserlis, 'Biometrika,' vol. 10, p. 893.

Indeed, the two theorems, that just given and the previous one,

$$1 - \frac{1 - R^2_{1.384...m}}{1 - R^2_{1.384...m}},$$

are, verbally expressed, identities, the latter having relation to standard deviations measured from planes in higher dimensioned space, i.e. to multiple "linear" regression—and the former to standard deviations measured from curved surfaces in higher dimensioned space, i.e. to multiple "skew" regression. The one theorem passes into the other as the skew regression surfaces become planes.

Unfortunately while the rule for finding H_{1.28...m} is quite simple, the arithmetic is very laborious. The next step in advance must be such a study of skew regression surfaces that we shall learn how to express the multiple correlation ratio in terms of total correlation ratios as we know how to express the multiple correlation coefficient in terms of total correlation coefficients. The first step in this direction has recently been taken by Isserlis in the memoir cited above.

On a Spectrum Associated with Carbon, in Relation to the Wolf-Rayet Stars.

By Thomas R. Merton, B.Sc. (Oxon.), Lecturer in Spectroscopy at University of London, King's College.

(Communicated by A. Fowler, F.R.S. Received June 3, 1915.)

The comprehensive investigations of Campbell* have shown that the spectra of the Wolf-Rayet stars contain in addition to lines due to hydrogen and helium, a number of lines which have not been identified with any spectrum which has hitherto been produced in the laboratory. Owing to the very diffuse character of the lines in the spectra of the Wolf-Rayet stars, accurate measurements of wave-length are impossible, and any identification of the kines with a terrestrial spectrum must, therefore, depend on the apparent coincidence of a relatively large number of lines with the spectrum produced in the laboratory.

^{* &#}x27;Astronomy and Astrophysics,' vol. 13, p. 448 (1894).

M. Wolf* has materially added to our knowledge in the more refrangible regions of the spectra of these stars, but in the less refrangible regions, few lines have been added to the list given by Campbell. In a recent investigation, Wright† has discussed the possible relations between the Wolf-Rayet stars and the planetary nebulæ.

In the spectra of these stars, the lines of the ζ Puppis series are very prominent, and from the high order of energy which is necessary to produce this series in the laboratory it might be expected that other lines in the Wolf-Rayet spectrum would be found in the enhanced lines of some terrestrial element.

Nicholson, in his remarkable theoretical investigations of the spectra of the nebulæ and the Wolf-Rayet stars, has concluded that the Wolf-Rayet spectrum is due to evolution products of the more simple atomic systems which are responsible for the nebular lines, and his suggested arrangement of the lines in series, somewhat resembling those ordinarily found, would appear to strengthen the possibility of producing the Wolf-Rayet spectrum in the laboratory.

The writer has recently observed a spectrum, apparently associated with carbon, of which the principal lines would appear to coincide with some of the most conspicuous lines in the Wolf-Rayet spectrum.

The spectrum was produced by passing heavy condensed discharges through vacuum tubes containing hydrogen at a moderately low pressure, and which were provided with graphite or carbon electrodes. The electrodes consisted either of pencil leads, which had been heated to a white heat and subsequently treated with boiling nitric and hydrochloric acids, or thin rods cut from a specially pure block of carbon and treated in the same way. The electrodes were attached to platinum wires, which were sealed into the vacuum tubes in the usual way. The tubes were exhausted by means of a Gaede mercury pump and a heavy discharge was passed during the process of exhaustion. Pure hydrogen was admitted by heating, in a Bunsen flame, a small palladium tube connected with the vacuum tube. The gas thus admitted was pumped out, and this operation was repeated several times in order to wash out completely any trace of other gases from the tube.

The vacuum tubes, when freshly prepared, showed only the spectrum of hydrogen with a trace of the Ångström carbon oxide bands, but after running the tube for some time the hydrogen spectrum disappeared and nothing remained but a very brilliant spectrum showing the Ångström bands. At the

^{* &#}x27;Sitz, Heidelberger Akad, Wiss.,' Abh. 14 and 22 (1913).

^{† &#}x27;Astrophys. Journ.,' vol. 2, p. 466 (1914). \$

¹ See 'Monthly Notices, R.A.S.,' vol. 75, 4, p. 340.

same time, carbon was deposited on the walls of the capillary; it was thus necessary to use end-on tubes for the spectroscopic observations. When excited by a condensed discharge, with a spark-gap in the circuit, the tubes showed the line spectrum of carbon and in the more refrangible region the multitude of lines, due to oxygen and the glass walls of the capillary, which appear in every low pressure vacuum tube excited in this way. The most characteristic lines, however, were a group in the yellow-green. In Table I are given the principal lines in this spectrum.

Table I.

Remarks.	, Intensity.	λ.
} Characteristic carbon pair.	8 9	6583 6578
J	. 8	58 36 - 7
	5	5812 0
	7	5801 4
5694 1 Ångström and Thalén.	10	5696 .0
u	8	5592 1
•	8	4651 6
	8	4850 4
•	10	4647 6
Very strong carbon line.	10	4267

With the exception of the very characteristic carbon lines at $\lambda\lambda$ 6583, 6578, and 4267, the lines included in this list are only those lines which are enhanced by very powerful discharges. Other lines recorded* as carbon lines were present, and also a pair at λ 5893 and a line at λ 6098, which, Prof. Fowler informs me, have long been regarded as unrecorded carbon lines in the South Kensington laboratories.

Lockyer, Baxandall, and Butler,† with similar conditions of powerful electric discharge, have observed the pair $\lambda\lambda 4650.8$ and 4647.6 in vacuum tubes containing compounds of carbon, and have attributed these lines to carbon; they have also drawn attention to the coincidence of this pair with lines in the spectrum of ϵ Orionis, and have suggested that they may possibly also account for the line $\lambda 4652$ of the Wolf-Rayet stars. These lines are undoubtedly identical with two lines given in the list.

A line has been recorded at λ56941 in the spectrum of carbon by Ångström and Thalén, but this line was not observed by Eder and Valenta or Gramont. Thalén has recorded lines in the spectrum of aluminium at

^{*} Kayser's 'Handbuch der Spektroscopie.'

^{† &#}x27;Roy. Soc. Proc.,' A, vol. 82, p. 532 (1909).

¹ Kayeer, loc. cit., vol. 5, p. 225.

 $\lambda\lambda$ 5695.5 and 5592.5, but it is extremely unlikely that these are identical with the lines observed in the vacuum tubes. Aluminium lines are a common impurity in the spectra of vacuum tubes excited by powerful discharges, the pair at $\lambda\lambda$ 3961.7 and 3944.2 being generally present. This may be due to the aluminium electrodes which are usually employed, or to the alumina (usually about 4 per cent.) contained in the glass. The lines at $\lambda\lambda$ 5696 and 5592 could not be obtained from vacuum tubes provided with aluminium electrodes and filled in the manner described. Moreover, in the spectrum from the tubes with carbon electrodes, these lines were not accompanied by the line λ 5722 of intensity 10, which is given in Thalén's list of aluminium lines. The new lines are diffuse in character, and are therefore difficult to measure.

It is dangerous to assume the origin of any lines obtained from vacuum tubes under these conditions of electric discharge, but it would appear justifiable provisionally to assign the lines observed to carbon, since it has not been found possible to obtain them in the absence of carbon.

The new lines are best developed when the walls of the capillary are well coated with the carbon deposit, and are strongly enhanced by powerful discharges, relative to the ordinary carbon lines. This is especially true of the group at $\lambda\lambda 5827$, 5812, 5801, which are scarcely visible with a weak condensed discharge. One may perhaps imagine a condition of still more powerful excitation, in which the spectrum of carbon would consist of the new lines, with faint lines at $\lambda\lambda 6583$, 6578, and 4267 as the sole surviving representatives of the ordinary carbon spark spectrum, since these are its most characteristic lines.

We may now compare these lines with the spectrum of the Wolf-Rayet stars. In Table II is given a list of Wolf-Rayet lines. It consists essentially of Campbell's (loc. cit.) list, with the following modifications:—

- (i) All lines due to hydrogen or helium have been omitted.
- (ii) Two lines observed by Merrill* have been included.
- (iii) Wright (loc. cit.) has pointed out that the band $\lambda 5813$ appears to vary in position in different stars, and in the star B.D. + 30°3639 can be seen to be composite, having components at $\lambda\lambda 5801$, 5812, 5828. These wavelengths have been substituted for the line $\lambda 5813$ in Campbell's list.

In Column I are given the Wolf-Rayet lines, and in Column II, under "vacuum tube," lines in the spectrum provisionally assigned to carbon.

For the line given by Campbell at λ 4273, Wolf (*loc. cit.*) finds in the stars 30°3639, 36°3956, and 35°4013 respectively the values $\lambda\lambda$ 4268·1, 4270, and 4269, a result which would indicate the possibility of this line being identical

^{* &#}x27;Lick Observatory Bulletin,' vol. 7, p. 129 (1913).

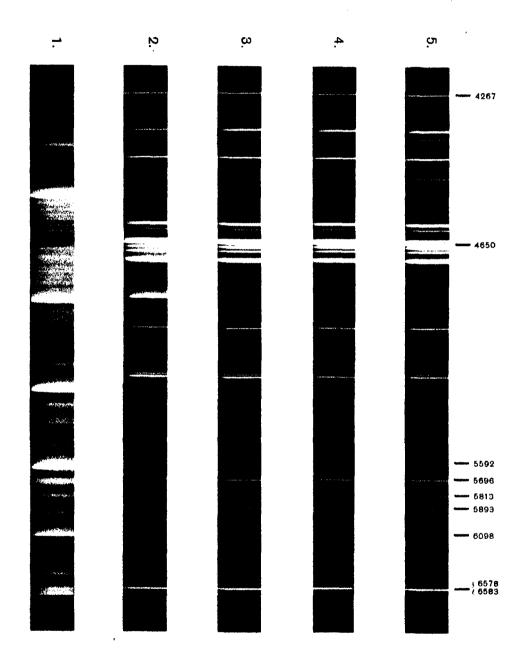
Table II.

I. Wolf-Rayet.	II. Vacuum tube.	I. Wolf-Rayet.	II. Vacuum tube.
λ.	*	λ.	
3583	[6583]	4615	
3548	↑6578 ∫	4596 4555	1
5848		4517 Strong	
1000	5826 -7	4509 Very strong	
ceta (pers campoen.	5812 0	4504 Strong	
SSOI Very strong	5801 -4	4498	
5698 Very strong	5696 0	4480	
5598 Strong 5472 Strong	5592 ·1	4466 Strong 4457	
1284]	4442 Strong	
5250		4416	
3181	1	486 9	
1940	¥	4884	
1787	[4651.6]	4318 4278	4267
1652 Very strong	4650 4	4260	7201
	4847 6	4228	
1086 Strong		4063 Strong	
1626 Strong	1	-	

with the carbon line λ 4267. Campbell's (loc. cit.) results would appear to suggest a common origin for the lines λλ 5813, 5693, 5593, 4650, which in almost every case occur together. On the other hand, the visual intensity curves of the spectra of different stars* show that the relative intensities of these lines vary considerably in different stars. Similar variations of intensity can easily be produced in the lines observed in the vacuum tubes, the triplet at \$\infty 4650 being produced with comparatively weak condensed discharges. The line $\lambda 5696$ is brought out with more powerful discharges, whilst the group $\lambda\lambda$ 5827, 5812, 5801, is strongly developed only by the most intense It will thus be seen that a considerable proportion of the stronger Wolf-Rayet lines are apparently coincident with lines in the vacuum tube spectrum. It cannot be claimed that the identity of the spectra has been fully established, but the results would appear to warrant the suggestion that the Wolf-Rayet lines in question may possibly be due to the same origin as the spectrum which has been described, and which is probably associated with carbon.

I should like to express my best thanks to Prof. Fowler for the valuable advice which he has given me.

In the plate, Nos. 1, 2, 3, 4, and 5 represent a series of the spectra obtained from a vacuum tube with successively increasing intensity of electric



discharge. Thus No. 1 was obtained with an uncondensed discharge and No. 5 with a heavy condensed discharge. No. 2, with a moderate condensed discharge, shows lines of the ordinary carbon spark spectrum with $\lambda\lambda$ 4650 and 5696. In No. 3, the λ 5813 group and λ 5593 are just visible, whilst No. 5 shows these lines with considerable intensity; they are situated in a part of the spectrum to which the plates used are comparatively insensitive, and their photographic intensities are, in consequence, very small in comparison with their appearance in visual observations. In the more refrangible region, which in the plate was necessarily over exposed, strong lines due to oxygen, etc., from the walls of the tube are visible. The use of a filter to counteract the sensibility curve of the plate was only partly successful.

Hydrodynamical Problems Suggested by Pitot's Tubes.

By Lord Rayleigh, O.M., F.R.S.

(Received June 5, 1915.)

The general use of Pitot's tubes for measuring the velocity of streams suggests hydrodynamical problems. It can hardly be said that these are of practical importance, since the action to be observed depends simply upon Bernoulli's law. In the interior of a long tube of any section, closed at the further end and facing the stream, the pressure must be that due to the velocity (v) of the stream, i.e. $\frac{1}{2}\rho v^2$, ρ being the density. At least, this must be the case if viscosity can be neglected. I am not aware that the influence of viscosity here has been detected, and it does not seem likely that it can be sensible under ordinary conditions. It would enter in the combination ν/vl , where ν is the kinematic viscosity and l represents the linear dimension of the tube. Experiments directed to show it would therefore be made with small tubes and low velocities.

In practice a tube of circular section is employed. But, even when viscosity is ignored, the problem of determining the motion in the neighbourhood of a circular tube is beyond our powers. In what follows, not only is the fluid supposed frictionless, but the circular tube is replaced by its two-dimensional analogue, i.e. the channel between parallel plane walls. Under this head two problems naturally present themselves.

The first problem proposed for consideration may be defined to be the flow

of electricity in two dimensions, when the uniformity is disturbed by the presence of a channel whose infinitely thin non-conducting walls are parallel to the flow. By themselves these walls, whether finite or infinite, would cause no disturbance, but the channel, though open at the finite end. is supposed to be closed at an infinite distance away, so that, on the whole, there is no stream through it. If we suppose the flow to be of liquid instead of electricity, the arrangement may be regarded as an idealised Pitot's tube, although we know that, in consequence of the sharp edges, the electrical law would be widely departed from. In the recesses of the tube there is no motion, and the pressure developed is simply that due to the velocity of the stream.

The problem itself may be treated as a modification of that of Helmholtz,* where flow is imagined to take place within the channel and to come to evanescence outside at a distance from the mouth. If in the usual notation† z = x + iy, and $w = \phi + i\psi$ be the complex potential, the solution of Helmholtz's problem is expressed by

$$z = w + e^w, \tag{1}$$

or
$$x = \phi - e^{\phi} \cos \psi$$
, $y = \psi + e^{\phi} \sin \psi$. (2)

The walls correspond to $\psi = \pm \pi$, where y takes the same values, and they extend from $x = -\infty$ to x = -1. Also the stream-line $\psi = 0$ makes y = 0, which is a line of symmetry. In the recesses of the channel ϕ is negative and large, and the motion becomes a uniform stream.

To annul the internal stream we must superpose upon this motion, expressed say by $\phi_1 + i\psi_1$, another of the form $\phi_2 + i\psi_2$ where

$$\phi_2 + i\psi_2 = -x - iy.$$

In the resultant motion,

$$\phi = \phi_1 + \phi_2 = \phi_1 - x, \qquad \psi = \psi_1 + \psi_2 = \psi_1 - y,$$

so that

$$\phi_1 = \phi + x, \qquad \psi_1 = \psi + y,$$

and we get

$$0 = \phi + e^{\phi + x} \cos(\psi + y), \qquad 0 = \psi + e^{\phi + x} \sin(\psi + y), \tag{3}$$

whence
$$x = -\phi + \log \sqrt{(\phi^2 + \psi^2)}, \quad y = -\psi + \tan^{-1}(\psi/\phi)$$
 (4)

or, as it may also be written,

$$z = -w + \log w. \tag{5}$$

It is easy to verify that these expressions, no matter how arrived at, satisfy

^{* &#}x27;Berlin Monateber.,' 1868; 'Phil. Mag.,' vol. 36, p. 337 (1868). In this paper a new nath was opened.

[†] See Lamb's 'Hydrodynamics,' § 66.

the necessary conditions. Since x is an even function of ψ , and y an odd function, the line y=0 is an axis of symmetry. When $\psi=0$, we see from (3) that $\sin y=0$, so that y=0 or $\pm \pi$, and that $\cos y$ and ϕ have opposite signs. Thus when ϕ is negative, y=0; and when ϕ is positive, $y=\pm \pi$. Again, when ϕ is negative, x ranges from $+\infty$ to $-\infty$; and when ϕ is positive x ranges from $-\infty$ to -1, the extreme value at the limit of the wall, as appears from the equation

$$dx/d\phi = -1 + 1/\phi = 0,$$

making $\phi = 1$, x = -1. The central stream-line may thus be considered to pass along y = 0 from $x = \infty$ to $x = -\infty$. At $x = -\infty$ it divides into two branches along $y = \pm \pi$. From $x = -\infty$ to x = -1, the flow is along the inner side of the walls, and from x = -1 to $x = -\infty$ back again along the outer side. At the turn the velocity is of course infinite.

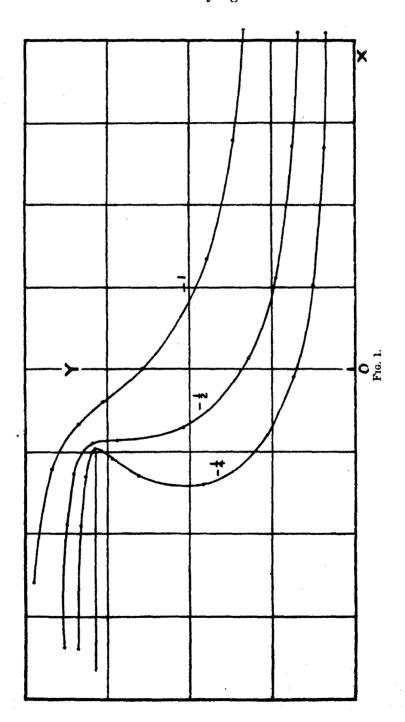
We see from (4) that when ψ is given the difference in the final values of y, corresponding to infinite positive and negative values of ϕ , amounts to π , and that the smaller is ψ the more rapid is the change in y.

The corresponding values of x and y for various values of ϕ , and for the stream-lines $\psi = -1$, $-\frac{1}{2}$, $-\frac{1}{4}$, are given in Table I, and the more important parts are exhibited in the accompanying plots (fig. 1).

 $\psi = -1$. $\psi = -\frac{1}{2}$. 4 = -1. φ. x. y. x. y. . y. 12:31 - 10 1 .100 12 .303 0.2750 12 .30 0.550 0.8000 6.614 6.63 1 '198 - 5 6.610 0.600 - 8 - 2 4 .15 1 .822 4 102 0 .8888 0.665 4 112 1 '464 2 .701 0.8745 2.728 0.745 2.80 1 1.080 0 .495 1 .111 0.964 1 .35 1 .785 - 0.50 0.081 0.714 0.158 1.285 -0.790 1 .085 0 .25 0.00 2 .571 0.00 -1.3861.821 -0.6982:071 -12902 606 0.25 -0.847 2 .681 0 .888 3 .085 -1 '081 2 .928 0.50 -0.970 8 -147 -0.888 3 178 0.658 3 .856 1.0 1 195 2 .0 -1 '299 8 .267 -1.2778 .678 8 . 397 8.0 -- 1 '898 8 .308 -1 '888 8 477 2 584 8 .897 40 5 ·0 -3 389 8 .842 -8 .886 3 .542 7 .692 4 042 10.0 -7 1897 8 .867 20.0 -17 '00 4 .002

Table I.

In the second form of the problem we suppose, after Helmholtz and Kirchhoff, that the infinite velocity at the edge, encountered when the fluid adheres to the wall, is obviated by the formation of a surface of discontinuity.



where the condition to be satisfied is that of constant pressure and velocity It is, in fact, a particular case of one treated many years ago by Prof. Love, entitled "Liquid flowing against a disc with an elevated rim," when the height of the rim is made infinite.* I am indebted to Prof. Love for the form into which the solution then degrades. The origin O' (fig. 2) of x+iy or z is taken at one edge. The central stream-line ($\psi=0$) follows the line of symmetry AB from $y=+\infty$ to $y=-\infty$. At $y=-\infty$ it divides, one half following the inner side of the wall CO' from $y=-\infty$ to y=0, then becomes a free surface O'D from y=0 to $y=-\infty$. The connection between z and w ($=\phi+i\psi$) is expressed with the aid of an auxiliary variable θ . Thus

$$z = \tan \theta - \theta - \frac{1}{4} i \tan^2 \theta - i \log \cos \theta, \tag{6}$$

$$w = \frac{1}{2} \sec^2 \theta. \tag{7}$$

If we put $\tan \theta = \xi + i\eta$, we get

$$w = \frac{1}{4} (1 + \xi^2 - \eta^2 + 2i\xi\eta),$$

so that

hat
$$\phi = \frac{1}{4} (1 + \xi^2 - \eta^2), \quad \psi = \frac{1}{2} \xi \eta.$$
 (8)

We find further (Love),

$$z = \xi + i\eta + \frac{1}{2}\xi\eta - \frac{i}{4}(\xi^2 - \eta^2) - \frac{1}{2}\tan^{-1}\frac{2\xi}{1 - \xi^2 - \eta^2} - \frac{1}{2}\tan^{-1}\frac{2\xi\eta}{1 + \xi^2 - \eta^2} + \frac{i}{2}\log\{(1 - \eta)^2 + \xi^2\}$$
(9)

so that

$$x = \xi + \psi + \frac{1}{2} \tan^{-1} \frac{2\xi}{\eta^2 + \xi^2 - 1} + \frac{1}{2} \tan^{-1} \frac{4\psi}{\eta^2 - \xi^2 - 1}, \tag{10}$$

$$y = \eta - \frac{1}{4} (\xi^2 - \eta^2) + \frac{1}{2} \log \{ (1 - \eta)^2 + \xi^2 \}$$
 (11)

The stream-lines, corresponding to a constant ψ , may be plotted from (10), (11), if we substitute $2\psi/\xi$ for η and regard ξ as the variable parameter. Since by (8)

 $\phi = \frac{1}{4}(1+\xi^2) - \psi^2/\xi^2$, $d\phi/d\xi = \frac{1}{2}\xi + 2\psi^2/\xi^3$,

there is no occasion to consider negative values of ξ , and ϕ and ξ vary always in the same direction.

As regards the fractions under the sign of \tan^{-1} , we see that both vanish when $\xi = 0$, and also when $\xi = \infty$. The former, viz., $2\xi \div (4\psi^2/\xi^2 + \xi^2 - 1)$, at first + when ξ is very small, rises to ∞ when $\xi^2 = \frac{1}{2} \{1 \pm \sqrt{(1-16\psi^2)}\}$, which happens when $\psi < \frac{1}{4}$, but not otherwise. In the latter case the fraction is always positive. When $\psi < \frac{1}{4}$, the fraction passes through ∞ , there changing sign. The numerically least negative value is reached when $\xi^2 = \frac{1}{2} \{\sqrt{(1+48\psi^2)} - 1\}$. The fraction then retraces its entire course, until

^{* &#}x27;Camb. Phil. Proc.,' vol. 7, p. 185 (1891).

it becomes zero again when $\xi = \infty$. On the other hand the second fraction, at first positive, rises to infinity in all cases when $\xi^2 = \frac{1}{2} \{ \sqrt{(1+16\psi^2)} - 1 \}$, after which it becomes negative and decreases numerically to zero, no part of its course being retraced. As regards the ambiguities in the resulting angles, it will suffice to suppose both angles to start from zero with ξ . This choice amounts to taking the origin of x at O, instead of O'.

When ψ is very small the march of the functions is peculiar. The first fraction becomes infinite when $\xi^2 = 4\psi^2$, that is when ξ is still small. The turn occurs when $\xi^2 = 12\psi^2$, and the corresponding least negative value is also small. The first \tan^{-1} thus passes from 0 to π while ξ is still small. The second fraction also becomes infinite when $\xi^2 = 4\psi^2$, there changing sign, and again approaches zero while ξ is of the same order of magnitude. The second \tan^{-1} thus passes from 0 to π , thereby completing its course, while ξ is still small.

When $\psi=0$ absolutely, either ξ or η , or both, must vanish, but we must still have regard to the relative values of ψ and ξ . Thus when ξ is small enough, x=0, and this part of the stream-line coincides with the axis of symmetry. But while ξ is still small, x changes from 0 to π , the new value representing the inner face of the wall. The transition occurs when $\xi=2\psi, \eta=1$, making in (11) $y=-\infty$. The point O' at the edge of the wall $(x=\pi,y=0)$ corresponds to $\xi=0, \eta=0$.

For the free part of the stream-line we may put $\eta = 0$, so that

$$x = \xi + \frac{1}{2} \tan^{-1} \frac{2\xi}{\xi^2 - 1} + \frac{\pi}{2} = \xi - \tan^{-1} \xi + \pi, \tag{12}$$

where $\tan^{-1} \xi$ is to be taken between 0 and $\frac{1}{2}\pi$. Also

$$y = -\frac{1}{4}\xi^2 + \frac{1}{2}\log(1+\xi^2). \tag{13}$$

When & is very great,

$$x = \xi + \frac{1}{2}\pi, \qquad y = -\frac{1}{2}\xi^2, \tag{14}$$

and the curve approximates to a parabola.

When ξ is small,

$$x - \pi = \frac{1}{3} \xi^3, \quad y = \frac{1}{4} \xi^2, \tag{15}$$

so that the ratio $(x-\pi)/y$ starts from zero, as was to be expected.

The upward movement of y is of but short duration. It may be observed that, while $dx/d\xi$ is always positive,

$$\frac{dy}{d\xi} = \frac{\xi (1 - \xi^2)}{2(1 + \xi^2)},\tag{16}$$

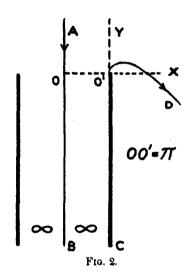
which is positive only so long as $\xi < 1$. And when $\xi = 1$,

$$x-\pi = 1 - \frac{1}{4}\pi = 0.2146, \quad y = -\frac{1}{4} + \log 2 = 0.097.$$

Some values of x and y calculated from (12), (13) are given in Table II, and the corresponding curve is shown in fig. 3.

Table II.— $\psi = 0$	0.
-----------------------	----

ξ.	. x .	у.	E .	r.	y.
0·0	8 ·142	0	2 ·5	4 ·451	- 0 ·571
0·5	8 ·178	+ 0 ·050	8 ·0	4 ·892	- 1 ·098
1·0	3 ·866	+ 0 ·097	4 ·0	5 ·816	- 2 ·583
1 ·5	3 ·659	+ 0 · 027	5 ·0	6 768	- 4 ·62
2 ·0	4 ·084	- 0 · 195	20 ·0	21 621	-97 ·00



It is easy to verify that the velocity is constant along the curve defined by (12), (13). We have

$$\frac{dx}{d\phi} = \frac{\xi^2}{1+\xi^2} \frac{d\xi}{d\phi} \,, \qquad \frac{dy}{d\phi} = \frac{\xi}{2} \frac{1-\xi^2}{1+\xi^2} \frac{d\xi}{d\phi} \,,$$

and when $\psi = 0$,

$$\phi = \frac{1}{4}(1+\xi^2), \qquad d\phi/d\xi = \frac{1}{2}\xi.$$

Thus

$$\frac{dx}{d\phi} = \frac{2\,\xi}{1+\xi^2}, \qquad \frac{dy}{d\phi} = \frac{1-\xi^2}{1+\xi^2},$$

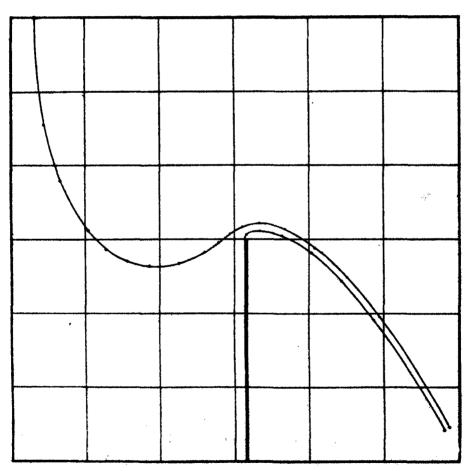
 $(dx/d\phi)^2 + (dy/d\phi)^2 = 1.$ (17)and

The square root of the expression on the left of (17) represents the reciprocal of the resultant velocity.

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Table III.— $\psi = \frac{1}{10}$.

ξ.	x.	y.	ξ.	r,	y.
0	0	øc .	0 40	2 .9667	+0.076
0.02	0 1667	9 .008	0 .50	3 .0467	0.180
0.10	0 .2995	8 008	0.460	3 · 1089	0.162
0.13	0 4668	1 .585	0.80	3 ·2239	0 - 198
0.15	0.6725	0 .766	1.00	8 · 8454	0 207
0.17	1 .0368	+0.109	1.50	3 -6947	+0.125
0.18	1 2977	-0.143	2 .00	4.0986	-0.112
0.19	1 5907	-0.804	2 50	4 .5234	-0.501
0.20	1 .8708	-0.370	3.00	4 .9725	-1 .032
0.22	2 2828	-0.881	4 00	5 .9089	-2.536
0.25	2 .5954	-0.195	6 .00	7 .8305	-7 161
0.80	2 8036	-0.047			



F10. 3.

When ψ differs from zero, the calculations are naturally more complicated. The most interesting and instructive cases occur when ψ is small. I have chosen $\psi = 1/10$. The corresponding values of ξ , x, and y are given in Table III, calculated from equations (10), (11), and a plot is shown in fig. 3.

As in the former problem, where the liquid is supposed to adhere to the walls notwithstanding the sharp edges, the pressure in the recesses of the tube is simply that due to the velocity at a distance. At other places the pressure can be deduced from the stream-function in the usual way.

Observations on the Fluorescence and Resonance of Sodium Vapour.—II.

By the Hon. R. J. STRUTT, Sc.D., F.R.S., Professor of Physics, Imperial College, South Kensington.

(Received June 12, 1915.)

[PLATE 8.]

§ 1. Introduction.

Prof. R. W. Wood has made many interesting observations on the fluorescence of sodium vapour. They are conveniently summarised in his 'Physical Optics' (MacMillan, 1911). The fluorescent spectra he has obtained are apparently connected with the banded absorption spectrum of dense sodium vapour. If white light is employed, this banded absorption spectrum is re-emitted completely as a fluorescent emission spectrum. If monochromatic light is used, a portion only of the complete band spectrum is emitted, this portion consisting of a moderate number of lines approximately equally spaced along a normal spectrum, and including a line coincident with the exciting line.

These observations on the band spectrum are of great interest and importance, but observations on the line spectrum of sodium, in absorption and in fluorescence, are more within the range of theoretical discussion at the present time.

The line spectrum is observed in absorption and in fluorescence at a density of sodium vapour small compared with that needed for the band spectrum.

If a beam of white light traverses such vapour, the D line and the other lines of the same series in the ultra-violet are seen in absorption. At the

same time there is a lateral re-emission of the D line, discovered by Wood, and called by him resonance radiation. The first paper of the present series* dealt with this resonance radiation. It is excited most conveniently not by white light but by sodium light, which contains the only effective constituent of white light.

The D line is the first member of a series of lines known as the principal series of sodium. The second line is at wave-length 3303 in the ultra-violet. The lines of this series up to a very high number can be seen in absorption, and since, in the case of the D line, the whole of the absorbed light quantitatively reappears in resonance radiation,† it would seem at first sight very probable that resonance radiation would also be observed at wave-length 3303, and at all the other lines of the Principal series.

The question arises also, would stimulation by a higher member of the series give rise to emission of a lower member? For instance would stimulation by λ 3303 give rise to D light? This question is not new. It has been proposed by Prof. R. W. Wood, and he has looked for such an effect, with negative results.\\$\text{\text{There}}\$ There was no doubt, however, that if anything of the kind could be observed, the fact would be important for the theory of spectrum series. For this reason I have made a fresh effort, which has had a successful issue.

§ 2. Excitation of D Light by \(\lambda\) 3303.

In planning the experiments, a source was looked for which would give a sharp and narrow line of great intensity at wave-length 3303. Preliminary experiments with a salted Meker flame showed that this source was extremely poor in the radiation desired. An oxy-hydrogen sodium flame might have done better, but I had recourse to a sodium vacuum arc, in quartz, which gave the line 3303 in equal intensity to the D line, measuring the intensity by the action on ordinary (not orthochromatic) plates.§

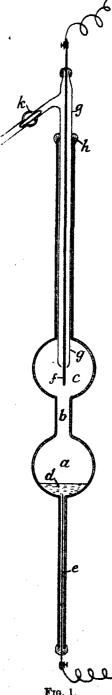
The silica envelope of the lamp (fig. 1) consists of two bulbs, a, c, each of 50 c.c. capacity, joined by a tube b, about 13 mm. inside diameter. The cathode is a pool of molten sodium d, and contact is made to it by an iron wire c, which passes out through a narrow quartz tube into which it is

^{* &#}x27;Roy. Soc. Proc.,' A, vol. 91, p. 388 (1915).

⁺ Dunoyer and Wood, 'Phil. Mag.' [VI], vol. 27, p. 1025 (1914).

^{‡ &#}x27;Phil. Mag.' [VI], vol. 18, p. 533 (1909). In this paper it is shown that excitation of dense sodium vapour by the group of zinc lines in the neighbourhood of λ 3303 gives rise to an ultra-violet band spectrum. But no definite evidence is given of any re-emission of λ 3303, nor have I myself been able to observe this, as will appear.

[§] This measure of relative intensity has of course no scientific value. It is merely used for practical convenience in comparing different sources. An energy measure would be enormously more favourable to the D line.



cemented with sealing wax. The anode is an iron wire f about 3 mm. in diameter. It passes up the glass fitting gg, into which it is cemented; gg is cemented into the silica tube at h. A stopcock k provides for exhaustion. The constriction at the bottom of gg, where the wire f passes out, prevents too much distillation of sodium into the upper part of this tube.

This form of lamp, arrived at after repeated trials, is fairly satisfactory in use, lasting long enough for a considerable number of experiments. The large bulbs are a most important feature. The lower one allows of the effervescence of the molten sodium, which always occurs at first. The upper one serves a different purpose. The anode f gets red hot, and if space is not allowed round it, the surrounding silica gets so hot as to be rapidly acted on by the sodium, eventually cracking.

The lamp must be kept well exhausted, preferably by continuous action of a Gaede mercury pump. The sodium gives off much hydrogen, and if this is not continually removed the lamp gets very hot, and the silica is rapidly blackened by reduction. The current passed is about 5 ampères.

The lamp is started by warming it and connecting an induction coil to the sodium cathode, and to a wire twisted round the tube b. After prolonged use the silica gets brown. The lamp can then be dismounted, cleaned out with alcohol and water, and then with dilute hydrofluoric acid, which readily removes the reduced silicon. It can then be recharged with sodium, and is almost as good as new.

It may be mentioned that the lamp gave eight lines of the principal series of sodium with half an hour's exposure on a small quartz spectrograph. The D line was exceedingly brilliant, and the strongest salted flame looked a very pale object beside the lamp. The lines of the two subordinate series were also shown very beautifully, the series relation being conspicuous to the eye.

Such lamps show the resonance radiation of D light

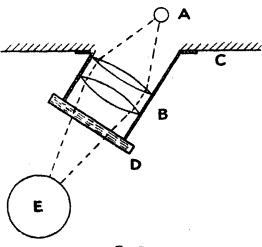
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incomparably better than any salted flame will do. The advantage lies not only in the brilliancy, but also in the narrowness of the D line. As Dunoyer has shown, only the central part of the broad line given by a flame is effective.

In studying the fluorescence produced by the line 3303, it is necessary to suppress the light due to the visual lines, particularly the D line. This was accomplished by a cell of cobalt blue uviol glass, filled with a dilute solution of nitrosodimethylaniline. This combination is very transparent to λ 3303, and suppresses everything in the visual region except a small part of the light of the red sodium line 6161. It is necessary to tolerate the latter, for if the nitroso solution is made strong enough to suppress it, serious loss of 3303 light is incurred. In practice not enough red light came through to cause inconvenience.

The light coming through the filter was examined with a quartz spectrograph. The only line on the plate was 3303. The visual spectrum showed only the red line 6161, and this could only be seen by directing the spectroscope straight at the lamp through the absorption cell.

The arrangements are shown in plan in fig. 2. The lamp is at A. It is



F1g. 2.

focussed by a quartz condenser B on the wall of the quartz flask E, the ultraviolet filter D intervening. B is set in the wall C of a dark cupboard, the axis of the lenses being inclined at about 60° to the wall, which makes the apparatus more accessible to an observer. The observations are made inside the cupboard.

E is a round-bottomed quartz flask of 100 c.c. capacity containing a little

sedium. It is connected by rubber tubing to a Gaede mercury pump, which is kept running, and which serves in addition to keep the sodium lamp A exhausted.

Before starting observations, the eyes are well rested in the dark. The bulb E is then well heated in a Bunsen flame, to nearly a red heat, so as to generate sodium vapour. When the lamp is started, the front surface of the bulb is seen to emit visual light. In the earlier experiments this was too faint for spectroscopic analysis, but it was examined by absorption methods.

First, a cell 1.2 cm. thick filled with saturated potassium bichromate solution held in front of the eyes was found to transmit it undiminished. This shows that the light must be in the yellow or red region of the spectrum. Secondly, the light was entirely cut off by substituting for the bichromate a strong solution of præsodymium nitrate. The latter solution transmits the red, but has an absorption band extending from $\lambda 5820$ to $\lambda 6020$. The D line at $\lambda 5890$ lies in this narrow region, and considering that the emission takes place from sodium vapour, there was practically no doubt that it did consist of D light.

In later experiments, under improved experimental conditions, the light was bright enough for its orange colour to be very conspicuous. Examined with a direct vision spectroscope it was found to be monochromatic, consisting entirely of D light. So far I have supposed the bulb to be quite hot, say at 350° C. In this case the 3303 light is not able to penetrate far into the sodium vapour, and consequently the D light excited is confined to the surface of the mass of vapour. As the bulb cools and the vapour diminishes in density, the excited D light gradually penetrates into the interior of the vessel, and fills it entirely. The light then slowly fades away as the vessel becomes cold.

These effects are exactly the same as are observed when D light is used as the exciting light. Possibly suspicion may arise that a trace of D light had been able to penetrate the ultra-violet filter and produced the observed effect. A simple test experiment entirely negatived this possibility. When a piece of ordinary plate glass, 1.2 cm. thick, was interposed in the path of the exciting beam so as to cut off ultra-violet light, the excited D light disappeared altogether.

§ 3. No Excitation of the D Lines by Other Kinds of Ultra-violet Light.

Another doubt may possibly remain. Granting that the excitation of D light is due to ultra-violet light, is it essential that this particular wavelength 3303 should be used? Would not any intense ultra-violet radiation serve?

To test this a mercury arc in quartz was substituted for the sodium arc. It gave very strong radiation through the ultra-violet filter, lighting up a piece of uranium glass much more brightly than the sodium lamp had done. It also caused the quartz wall of the bulb containing sodium to emit a little blue fluorescence, but when this was cut out by holding a bichromate solution before the eye, nothing remained: D light was not emitted. The strong ultra-violet mercury lines present were probably the groups about λ 3650 and λ 3130.

§ 4. Search for Evidence of Resonance Radiation at λ 3303.

It appears, therefore, that light energy of wave-length 3303 absorbed by sodium vapour is, in part at any rate, re-emitted as D light. Clearly then the relation found by Wood and Dunoyer for stimulation by D light,* that the whole of the absorbed energy reappears as energy of the same wavelength, cannot apply to the line 3303. It must be a peculiarity of the D line, distinguishing it from other members of the series.

The question arises, however, whether any part of the energy of λ 3303 is re-emitted at the same wave-length; whether, in other words, there is any resonance radiation of λ 3303.

An experiment was arranged as in fig. 3. In this case a cylindrical silica tube, about 2 cm. in diameter, kept in connection with the pump, contains the sodium vapour. Light of wave-length 3303 is incident perpendicularly upon it, as shown by the arrow. Some ultra-violet light is found to proceed obliquely from the point of incidence. It is focussed by a quartz lens B upon a fluorescent screen of uranium glass. The image is at D, and is shown by the fluorescence. This fluorescence must be viewed obliquely. If viewed in the prolongation of AD, yellow D light from A, stimulated in the way already described, enters the eye, and masks the fluorescence on the screen at D.

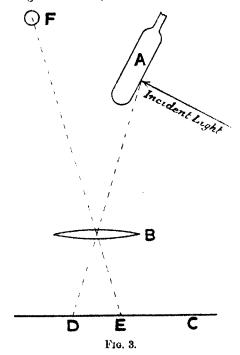
It is necessary to decide whether the ultra-violet light emitted from A is due to resonance radiation, or whether it is merely light scattered by the strike in the walls of the silica tube.

A comparison fluorescent patch was obtained at E by forming there the image of a small smokeless gas flame F. E was adjusted to be of the same brightness as D when the tube A was cold, and contained no sodium vapour, and when the solid sodium in the tube was out of the way of the incident light. On heating A so as to raise sodium vapour no increased brightness of the

^{* &#}x27;Phil. Mag.,' vol. 27, p. 1025 (1914).

[†] The arrangement adopted excludes specular reflection from the silica tube, as will be evident from fig. 3.

fluorescent patch at D could be observed. E was still a match for it. This proves that the resonance radiation of \$\lambda\$ 3303, if any, is but a small fraction of the light of this wave-length scattered by the walls of the vessel. A similar experiment was made with the same vessel but with D light as the exciting light. The ultra-violet filter was removed, a sheet of ordinary ground glass was substituted for the uranium glass at C, and a salted spirit flame for the smokeless gas flame at F. Starting with the sodium tube A cold, the yellow image at E was adjusted to equality with that at D. On heating the tube A, so as to raise sodium vapour, D became



many times brighter than E, owing to the resonance radiation, which entirely outshone the scattered light.

There is no reason to suppose that the fraction of the incident light scattered by the striæ in the quartz tube would be very different, whether this light consisted of D light or of λ 3303.

Assuming that the same fraction is scattered by the walls of the tube in each case, it follows from the experiments described that the resonance radiation is a very much smaller fraction of the exciting radiation for λ 3303 than for D light.*

* A tube with a window of clear optically worked quartz fused on would make it possible to push further the search for resonance radiation of λ 3303.

As already mentioned, the experiments of Dunoyer and Wood indicate that the whole of the absorbed D light is re-emitted as D light. My own experiments prove that this is not true for light of λ 3303. The interesting possibility remains for future investigation that not only a part but the whole of the absorbed energy of λ 3303 is re-emitted as D light. Such a result would, however, be difficult to reconcile with the quantum theory.

§ 5. Effect of One Component only of the Ultra-violet Doublet \(\lambda 3303. \)

The first ultra-violet sodium line, though hitherto spoken of as single, is in a fact a doublet like the D line. The components have wave-lengths, on the International system, of 3302.96 and 3302.35.* There are reasons for regarding these lines as belonging to different series: in fact, for regarding the principal series of sodium as really including two series. The series including D₁ and 3302.96, the less refrangible members of the respective doublets, are each split into four components in a magnetic field, while 3302.35 and D₂, the more refrangible members, are each split into six components. This point of view is strengthened by the observation of Wood and Dunoyer† that if sodium vapour is stimulated by the D₂ line, D₁ does not appear in the fluorescent radiation, which consists of D₂ light only.

It thus appeared of considerable interest to determine whether stimulation by the line 3302.96 would give rise to D_1 only, or whether it would give rise to D_2 (which may be regarded as belonging to a different series) as well. An accidental circumstance, to which attention has been drawn by Wood, made it possible to attack the question. This is the extreme nearness of certain zinc lines to wave-length 3303.

The zinc arc spectrum shows a doublet which lies inside the sodium doublet. The wave-lengths given by Kayser stand thus:

		Intervals.
Sodium		0.05
Zinc	3303∙05 ∫	บบอ
Zinc		0.01
Sodium	3302.49	0.21

Kayser's table has been compiled by critical collation of the data given by different observers. These observers have not of course felt any special interest in the exact relative position of the zinc and sodium lines mentioned, which has no importance except for the technique of the present investigation. It was thought therefore that direct comparison would give greater certainty

^{*} I quote these wave-lengths from the Table given at the end of Kayser's 'Spectro-scopy,' vol. 6.

^{† &#}x27;Phil. Mag.' [VI], vol. 27, p. 1018 (1914).



as so the exact intervals. The spectra were compared in the third order of a 10-foot Rowland grating, using a quartz vacuum are both for zinc and sodium. With short exposures the lines, especially in the case of sodium, were very fine and sharp. The intervals above mentioned were measured as 0.043 Ångström and 0.198 Ångström, in good agreement with the numbers adopted by Kayser.

In all the photographs there was some overlap of the images of 3303:10 (sodium) and 3303.05 (zinc). On the other hand there was definite separation of 3302.70 (sodium) and 3302.49 (zinc) by a narrow interval of clear glass. When there is separation, it is definite proof that the lines themselves do not overlap, but on the other hand an overlap of the photographic images is no proof of overlap of the lines themselves, for the images may be, and with any but the shortest exposures certainly are, broadened by irradiation. For this reason I have not been able to definitely establish from the spectrograms whether, and to what extent, 3303.05 (zinc) overlaps 3303.10 (sodium). It is scarcely doubtful that, as is known to be the case with mercury, the zinc lines broaden with increase of current. If therefore the zinc line 330305 does not overlap its sodium neighbour for small currents, an increase of the current will probably make it do so; on the other hand, up to 30 ampères at all events, the spectrograms still showed that there was no overlap of 3302.70 (zinc) and 3302:49 (sodium). Fig. 4 (Plate 8) shows an enlargement of a photograph taken with 30 ampères passed through the zinc lamp. The closer doublet in the middle is of course the zinc one, the sodium doublet appearing . above and below.

The net result of this study of the spectra is to show that there is a zinc line in practical coincidence with the less refrangible member of the sodium doublet, but no zinc line in coincidence with the more refrangible member. If we use a zinc arc to excite sodium vapour, we apply excitation at one line only of the doublet 3303.

The form of lamp which has been found useful for zinc vapour is shown in fig. 5. It is a slight modification of that used for sodium. The envelope of the lamp consists of two lengths of rough silica tube each about 13 mm, inside diameter and 30 cm. long, united by a short piece of clear silica tubing about 8 mm, inside diameter. The cathode is a layer of molten zinc d resting on an iron plug e, which of course must not fit the silica tube too tightly. A mica washer at f prevents the molten zinc running down below e. Connection is made to e by an iron wire g passing out through a glass fitting h,

^{*} Probably this could be done if the spectrograph were arranged with a suitable lens to form an enlarged image on the plate of the original grating image of the group sain.

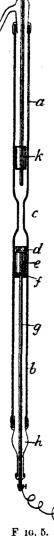
cemented with sealing wax. The anode k is also a loose iron plug, with a pointed end, as shown. The connection is brought out in the same way. A side tube l in the glass fitting provides for exhaustion.

The arrangements for the experiment are seen in plan in fig. 6. The zinc lamp is shown in section at A. The rays from it pass through the quartz condenser B set obliquely in the wall as before, then through the ultra-violet filter D, converging at E on to the wall of a quartz bulb containing sodium vapour. The rays impinge on the quartz bulb almost at grazing incidence, and set up a fluorescence of D light, as when the sodium lamp is used as a source of 3303 light. The intensityof this light depends very much on the current through the This is no doubt due to the fact that at small currents the zinc line is too narrow for any overlap with the sodium line. With larger currents such overlapping begins, and the vapour is stimulated. With currents of 4 ampères no D light is seen. Increasing the current to 6 ampères it can be seen, and identified by the absorption methods before described. At 15 ampères it is bright enough for spectroscopic examination. The current may be further increased up to 100 ampères, with a great increase in the fluorescent light, which is now, perhaps, as bright as a slightly salted flame. The zinc lamp, however, will only stand these currents for a few seconds. It has been found convenient to start up the lamp, and run it at, say, 6 ampères, by means of a regulating resistance. When all is ready for observation this resistance is shunted by a smaller one, so as to pass a heavy current for a short time. For the heaviest currents a fuse wire without other resistance is used in the shunt circuit, and allows the heavy current to pass for a few seconds only; enough, however, for observation. The lamp is not extinguished when the fuse melts in the shunt circuit, thus the observation can easily be repeated after replacing the fuse.

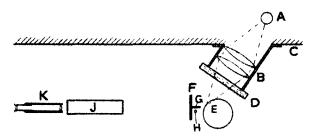
In order to decide whether one or both D lines were present, a special spectroscope was employed, consisting of slit, direct vision prism, and telescope. The slit, 1 mm. broad, is a fixed one, made in a brass sheet F. The slit itself is horizontal, and is in the plane of the diagram (fig. 6). A vertical strip of

is in the plane of the diagram (fig. 6). A vertical strip of brass G divides the length of the slit into two parts.

One of these parts (that towards the top of the page on the diagram) is backed by the fluorescent light of the sodium vapour in E. The other part



is backed by a minute soda flame H, which affords a comparison spectrum. This flame is simply a coal-gas flame burning from a drawn-out soda glass



F1g. 6.

jet, and turned down "to the blue." Its spectrum shows the D line superposed upon the Swan spectrum.

The prism used (indicated at J) is a powerful combination designed by Lord Rayleigh,* to whom I am indebted for the loan of it.

Ten right-angled flint glass prisms, with their refracting edges horizontal, are immersed in carbon disulphide, containing enough benzol to exactly compensate the deviation for D light. The combination is 20 inches long. It was mounted with its nearest end 48 inches from the slit, though represented much nearer in the figure, for convenience. Under these conditions the D lines in the comparison spectrum were seen well separated with the naked eye, but in the experiment a telescope K was used. It consisted of single convex lenses, object glass 5 inches and eyepiece $1\frac{1}{2}$ inches focal length, giving rather more than three-fold magnification.

With this amount of magnification the images lose nothing in brightness, while they gain in angular magnitude—always an advantage in dealing with very faint objects. The telescope tube was covered with phosphorescent paint near the eyepiece, which proved a convenience for quickly finding one's way to it in the dark.

The spectroscope thus arranged proved most satisfactory for resolving the D lines from a very faint source, and I do not think that it could be improved on for this purpose. The great advantage of the large dispersion is that a wide slit is admissible.

In making the observations the zinc lamp was started with a small current, the quartz bulb was heated, and the observer at the spectroscope

^{*}See his 'Collected Scientific Works,' vol. 1, p. 459, and vol. 4, p. 394.

got his eye rightly directed and focussed so as to see the D lines well in the comparison spectrum. He then knew exactly where to look for these lines in the usually fainter fluorescence spectrum, during the short time it was on. This use of a comparison spectrum is practically essential. It is strongly to be recommended in all spectroscopy of faint sources. At the first test, 100 ampères were passed for a moment, and both D lines were seen in equal intensity, as bright as the comparison spectrum, if not more so. In subsequent tests the current was reduced by successive stages down to 15 ampères. At this point the result was still the same, quite definite and distinct. With smaller currents than 15 ampères the fluorescent light was too faint for spectroscopy.

In all not less than a dozen observations were made, not all on the same day, and each one of them separately was conclusive as to the general result. I was not able to decide definitely which, if either, of the D lines was the brighter. In a flame D₂ is somewhat brighter than D₁, but in the spark no definite difference is recorded.

As already shown, stimulation is confined to the component 3303·10 at 30 ampères, and possibly for much larger currents still. Both the D lines appear in equal intensity at 15 ampères. There is, therefore, an ample margin of safety in saying that stimulation applied at one member only of the first ultra-violet doublet gives rise to emission of both the D lines.

§ 6. Search for Fluorescent Emission of the Subordinate Series Lines.

As stimulation at 3303 had proved capable of bringing out the D lines it seemed possible that it might also bring out the subordinate series lines. To look for these a zinc lamp was first used, loaded momentarily with 100 ampères.

The arrangements were as in fig. 6, except that instead of using the prism J and the telescope K, the slit was viewed without a telescope, through a much less dispersive direct vision bisulphide prism, the eye being only about 8 inches from the slit. The spectrum obtained in this way was short and bright. The swan spectrum of the little gas jet H served as an approximate guide for the eye, and the lines 5685 and 6157 of the first and second subordinate series specially looked for. No trace of them, or of any other line except the D line, could be seen in the fluorescent spectrum.

A second attempt was made, using the sodium lamp as a source of λ 3303. A quartz tube, 2 cm. diameter, was used to contain the vapour, and examined with an ordinary pocket spectroscope. In this case the brightness was perhaps somewhat less, but the observations could be made at leisure because the sodium lamp does not need to be heavily overloaded in order to

bring out the fluorescence. No trace of the subordinate series lines could be seen. The green one, 5685, at all events, could have been seen if it had had the same intensity relative to the D line as it had in the original sodium lamp. My colleague, Prof. Fowler, very kindly made these observations with me.

§ 7. Summary.*

- (1) Sodium vapour, illuminated by the second line of the principal series at wave-length 3303 in the ultra-violet emits the D line, which is the first member of that series, in fluorescence.
- (2) Stimulation by ultra-violet light in general does not cause emission of the 1) line.
- (3) If one member only of the ultra-violet doublet 3303 is stimulated, not one only, but both of the D lines are emitted, in about equal intensity.

This is an unexpected result, in view of the work of Wood and Dunoyer, who found that stimulation by D_2 light was unable to excite D_1 light.

(4) Stimulation at λ 3303 was not found to give rise to any observable resonance radiation of the same wave-length, nor to any observable emission of the subordinate series lines.

I have much pleasure in thanking my assistant, Mr. R. Thompson, for valuable help in carrying out the experiments.

* The chief results of this investigation were indicated in preliminary communications to 'Nature,' May 13 and June 3, 1915.

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The Influence of Gases on the Emission of Electrons and Ions from Hot Metals.

By O. W. RICHARDSON, M.A., D.Sc., F.R.S., Wheatstone Professor of Physics, University of London, King's College.

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As is well known, the saturation density i of the electron currents from hot bodies can be represented accurately by the formula

$$i = AT^{\frac{1}{2}}e^{-h/T}, \tag{1}$$

where T is the absolute temperature and A and b are constants characteristic of the substance. An equation of type (1) has been found to represent the currents not only from pure metals in a good vacuum but also when a gaseous atmosphere is present, provided the constants are given different Thus in general A and b are functions of the nature and pressure of the surrounding gas as well as of the hot metal. They are independent of T within the limits of temperature in which the formula is valid. the case of pure metals there is evidence that the formula is valid at all In certain cases the constants A and b are very sensitive to minute changes in the nature and pressure of the surrounding gaseous atmosphere. This is well shown by Langmuir's experiments on tungsten, where a slight trace of hydrogen changed the value of A by a factor of about 10^{12} and that of b from 5.5×10^{4} °C, to 11.5×10^{4} °C. In the case of platinum heated in an atmosphere of hydrogen, H. A. Wilson+ has shown that A and b are functions of the pressure of the hydrogen, and that the changed values of A and b are subject to the relation

$$b = c \log A + d, \tag{2}$$

where c and d are constants. In other words, the changes in the constants A and b caused by the admission of hydrogen are always of such a character that the change in $\log A$ divided by the change in b is invariant. In the present paper it is shown that a similar relation holds for the changes in the values of A and b for tungsten which are caused by traces of various gases. In fact it seems probable, in general, that when the emission of ions from metals is affected by the presence of gases, the changes in A and b are subject to a linear relation between b and $\log A$. There is evidence that the relation is independent of the particular gas used to

^{* &#}x27;Phys. Rev.,' vol. 2, p. 450 (1913).

^{† &#}x27;Phil. Trans.,' A, vol. 208, p. 247 (1908).

effect the changes, and that the law applies to the emission of positive ions as well as electrons from hot metals. In view of the complexity of the phenomena which may occur when metals at a high temperature are immersed in a gaseous atmosphere it seems unlikely that such a simple law will be exact for all the small changes in A and b which may arise; but the evidence is strong that it covers the main features of the phenomenon.

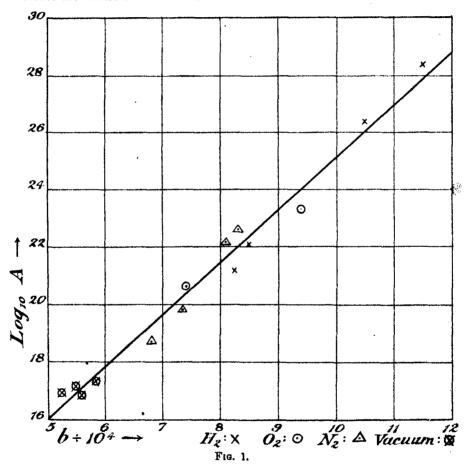
Let us consider the case of tungsten first. Langmuir (loc. cit.) has measured values of A and b from this substance both in the best attainable vacuum, similar to that in a Coolidge tube, and in a high vacuum to which small amounts of various gases have been added. The data obtained are shown in the following Table:—

Gas.	Pressure.	Α.	ь.
	mm, Hg.	E.S.U. per cm.2.	° C.
Vacuum		7.08×10^{16}	5 '25 x 10 ⁴
,	-	6.6×10^{16}	5.58×10^4
?? ?!	0.00007	10.2×10^{16}	5.55×10^{4}
Ĥъ	0.012	1.62×10^{21}	8.25×10^4
,,	0.0005	1 ·29 × 10 ²²	8.5×10^{4}
",	0.007	2.28×10^{28}	11.5×10^4
,,	0.0017	2.81×10^{26}	10.5×10^4
Ó _g		2 ·04 × 10 ²³	9.43×10^{4}
N_2	0 002	6.6×10^{19}	7.32×10^{4}
,,		5.0×10^{18}	6.82×10^{4}

The conditions were varying with the time in some of the experiments, so that in such cases the data are only approximate. It is clear from a glance at the figures for hydrogen that A and b are not definite functions of the pressure of this gas. The changes in the constants apparently caused by hydrogen are probably caused by some other substance introduced with it. Langmuir, who takes this standpoint, attributes them to traces of water vapour.

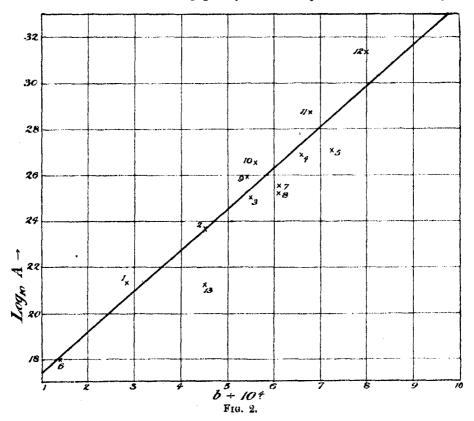
Although there is no relation between the values of either A or b and the pressure of the gas which appears to determine these values, there is a definite relation between all the corresponding values of A and b given in the Table. It will be noticed that the corresponding values of A and b always diminish or increase together. Thus a high value of A always corresponds to a high value of b, and vice versa. In fact, no matter which of the gases tested determines the values of the constants $\log A$ is a linear function of b. This is clearly shown in fig. 1, in which $\log_{10} A$ is plotted against the corresponding value of $b \div 10^4$. The figure contains all the data given in the Table, and some others in addition. In fact, it contains all the

values of A and b for tungsten which are at present available, and which there is reason to consider reliable. The deviations of the points from the straight line may be real, or they may be due to erroneous determinations of the constants owing to the time changes already referred to, or to other causes. It will be noticed that the pure tungsten in the best vacuum gives the least values both of A and b, the effect of gaseous contamination being to increase the values of both constants.



It is interesting to compare these values for tungsten with similar data for platinum in hydrogen and other gases. In fig. 2 I have collected all the available corresponding values of A and b, which there is reason to believe trustworthy, as well as some others, for which the nature of the probable error may be forecasted. Nos. 1, 2, 3, 4, and 5 are the observations which led H. A. Wilson (*loc. cit.*) to conclude that the change in log A caused by

hydrogen was proportional to the simultaneous change in b. No. 1 is for H_2 at 133 mm., No. 2 for H_2 at 0.112 mm., No. 3 for H_2 at 0.0013 mm., and Nos. 4 and 5 for a good air vacuum. No. 7 is from data given by Deininger* for a vacuum, and No. 8 from data given by Horton† in an atmosphere of helium at a pressure of a few millimetres. No. 9 is the first determination of A and b which was made by the writer‡; the conditions probably corresponded with those for a hydrogen vacuum of about 0.001 mm. Nos. 10, 11, and 13 are taken from a later paper by the writer.§ No. 10 is for nitrogen



at 2.8 mm., No. 11 for oxygen at 2 mm., and No. 13 for air at 760 mm. No. 12 is a preliminary value given by Langmuir (*loc. cit.*) under high vacuum conditions. So far as one can judge, this experiment should correspond to superior freedom from gaseous contamination.

^{* &#}x27;Ann. der Physik,' vol. 25, p. 285 (1908).

^{† &#}x27;Phil. Trans.,' A, vol. 207, p. 149 (1907).

^{; &#}x27;Camb. Phil. Proc.,' vol. 11, p. 286 (1901).

^{§ &#}x27;Phil. Trans.,' A, vol. 207, p. 1 (1906).

Considering all the points simply as they stand, the divergence from the straight line drawn is considerably greater than the corresponding deviation of the tungsten points shown in fig. 1. The agreement is, however, very much improved if the conditions affecting the different determinations, which are by no means of equal value, are intelligently considered. Thus Nos. 10 and 11 are believed to be affected by the occurrence of ionisation by collision. This makes A too big without changing b. Again No. 13 is believed to be affected by lack of saturation. If the currents are fairly small fractions of the saturation values A will be too small and b unaltered. These objections to Nos. 10, 11, and 13 were pointed out when the original data were published. On these grounds we should expect Nos. 10 and 11 to be above and No. 13 below the line, as in fact is the case. No. 9 is a very old observation and its distance from the line might be due to a number of causes. No. 5 is deduced from a small number of determinations of very small currents which extend over a short stretch of temperature; so that the possible error of measurement in this case must be quite considerable. No. 12 is given by Langmuir as only a preliminary determination, and further investigation may change its position considerably. As regards Nos. 7 and 8 there does not seem to be any obvious criticism one can offer; but they are not very far from the line, and it is possible that the true position of this should be a little to the right of that in which it has been drawn.

We see then that in platinum as well as tungsten there is a correspondence between the values of A and b, so that large values of A correspond to large values of b, and conversely. There is, however, one important difference between the two metals. In tungsten the pure metal has small values of the constants, which are increased by gaseous contaminants, whereas pure platinum appears to be characterised by high values of the constants, which are reduced by the presence of gases. It is possible that traces of hydrogen are responsible for all the changes observed with platinum, but that is a point which I do not wish to discuss in the present paper, the object of which is to consider corresponding changes in A and b without reference to the processes causing them. Since the changes observed with platinum and tungsten are similar, but in opposite directions, it is natural to try to attribute them to similar causes acting in opposite senses in the two metals.

Theory of the Effect of Gases on the Emission Constants.

The theory of the effect of hydrogen on electron emission from platinum has been considered at length by H. A. Wilson.* In the present paper I

^{* &#}x27;Phil. Trans.,' A, vol. 208, p. 247 (1908).

shall consider the effect of contamination on the emission constants in general from a somewhat different standpoint. It has been found empirically that the emission from pure metals either in a vacuum or in equilibrium with a gaseous atmosphere can be represented by the formula

$$i = AT^{\frac{1}{4}}e^{-b/T}.$$
 (1)

There is a certain amount of doubt about the exact value of the index of T in the factor $T^{\frac{1}{2}}$ in this formula, as the particular value $\frac{1}{2}$ may be replaced by any number between 0 and +2 without appreciably affecting the agreement of the formula with the experimental numbers, provided somewhat different values of the constants A and h are taken. We shall, however, disregard this point and assume (1) to hold, as the values of the constants we are dealing with are based on the assumption that (1) is valid. In addition to equation (1) there are a number of related equations* which may be deduced by the application of the principles of thermodynamics to electron emission. In considering these it is more convenient to deal with the number n of electrons per cubic centimetre of the space outside the body which are in equilibrium with it at the temperature T, instead of the saturation current. These quantities are related by the equation

$$i = ne(kT/2\pi m)^{\frac{1}{2}}, \tag{3}$$

where ϵ is the charge and m the mass of an electron and k is Boltzmann's constant. The only assumptions involved in the relations referred to are (1) the reversibility of the phenomena, (2) the two laws of thermodynamics, and (3) the applicability of the law of a perfect gas to very attenuated electron atmospheres. The results must, therefore, possess a very high degree of certainty.

The proofs of these relations hitherto given only apply to the case in which gases are absent. It is thus necessary to modify them somewhat in order to obtain results which will be valid when gases are present and may affect the emissions either by reacting with the electrons or contaminating the surfaces. For purposes of calculation a contaminated surface may be regarded as a pure surface covered with a contaminated layer of uniform composition to a small but finite thickness. This will probably give a fair representation of the facts unless the layer of actual contamination is excessively thin. In that case the superficial properties of the contaminated material might become somewhat indefinite. The proposed treatment practically amounts to considering the pure metal as being covered with a thin layer of another metal having the properties of the contaminated

* Cf. 'The Electron Theory of Matter,' Chap. XVIII, Cambridge University Press, 1914.

surface. It is evidently necessary to take account of the existence of the contact potential difference and of the Peltier electromotive force between the pure and contaminated materials.

Bearing this in mind, a calculation similar to that in 'Phil. Mag.,' vol. 24, p. 619 (1912), shows that

$$n = A_1 e^{\int \mathbf{w}/kT^2 \cdot dT}, \tag{4}$$

where A_1 is a constant independent of T and w is the change of energy when one electron passes from the interior of the contaminated material to the space outside. In carrying out the calculation a virtual displacement may be imagined to be produced in a closed cylinder filled with the gas under consideration by a piston permeable to the gas but not to the electrons. The base of the cylinder consists of the emitting material. With this arrangement the only work done is caused by the partial pressure of the electrons on the piston. On account of the integral in the exponent of e in (4) this relation does not appear to be well adapted to a discussion of the changes, in A and e in equation (1), which are caused by gases. Another disadvantage of (4) is that it gives e in terms of the value of e for the contaminated material, and this quantity is not directly accessible to experiment.

Another relation involving the specific heat of electricity in the metal is given in the 'Electron Theory of Matter,' p. 448. The proof may be extended to cover the case when gases are present by covering the bodies A and A' with a definite layer of the contaminated material in equilibrium with the gas, as already outlined. The difference of potential V'-V now includes the contact potential between the two contaminated surfaces. Before equalising the potentials in the manner described in the calculations referred to, the electrons are separated from the gas by drawing them through a semi-permeable membrane which stops the gas. energy, ξ per electron, may be supposed to be involved in this process without affecting the final results, which are thus valid even if the electrons enter into combination with the gas molecules. The only other change in the calculation is the introduction of the change in the energy of an electron on passing the interface between the contaminated and the pure surfaces, which corresponds to the Peltier effect. Proceeding, except for these changes, in the manner of the calculation referred to, we find

$$n = \operatorname{CT}^{1/(\gamma-1)} e^{-\left[(w+\eta)/k\mathbf{T} + (\epsilon/k) f^{\mathbf{T}} \operatorname{S/T} \cdot d\mathbf{T}\right]}. \tag{5}$$

where C is a universal constant, γ is the ratio of the two specific heats for the electron gas, w is the energy change at liberation of an electron from the contaminated material, η is the energy change when an electron passes from the pure to the contaminated material and corresponds to the Peltier effect, ϵ is the electronic charge, and S is the specific heat of electricity for the pure material. If we consider another temperature, T', for which the values of the corresponding quantities are denoted by dashes,

$$n' = CT' \frac{1}{(\gamma - 1)} e^{-\frac{1}{(\gamma' + \eta')/kT} + (\tau/k) \int T' S/T \cdot dT};$$
 (6)

so that $n/n' = (T/T')^{1/(\gamma-1)} e^{-[(w+\eta)/kT - (w'+\eta')/kT' + (\epsilon/k)]} \int_{T'}^{T} S/T \cdot dT}$. (7)

But by a well-known thermo-electric result

$$\frac{\eta}{T} - \frac{\eta'}{T'} + \epsilon \int_{T'}^{T} \frac{S}{T} dT = \epsilon \int_{T'}^{T} \frac{S_1}{T} dT, \tag{8}$$

where S_1 is the specific heat of electricity for the contaminated material. Thus

$$n/n' = (T/T')^{1/(\gamma-1)} e^{-\left[w/kT - w'/kT' + (\epsilon/k)\right]} \int_{T'}^{T} S_t/T \cdot dT. \tag{9}$$

From (4)
$$n/n' = e^{\int_{\mathbf{T}'}^{\mathbf{T}} w_i k \mathbf{T}^2 \cdot d\mathbf{T}_i}$$
 (10)

hence, by comparison with (9),

$$\frac{\partial w}{\partial \Gamma} = \epsilon S_1 - \frac{k}{\gamma - 1}. \tag{11}$$

It appears from this that if w for a contaminated material varies considerably with temperature, the specific heat of electricity in such a material may be expected to have abnormally large values.

If n_1 , w_1 and η_1 are the values of these quantities for the pure material at temperature T,

$$n_1 = CT^{1/(\gamma-1)} e^{-[(w_1+\eta_1)/kT + (\epsilon/k) \int^T S/T \cdot dT]},$$
 (12)

 η_1 is obviously zero, but the equations are more symmetrical if it is retained. By comparison with (11)

 $n/n_1 = e^{-[w+\eta-(w_1+\eta_1)]/kT}, (13)$

By a known result,* $w+\eta-(w_1+\eta_1)$ is equal to ϵV_1 where V_1 is the contact potential difference between the pure and contaminated surfaces. Thus, if i and i_1 are the saturation currents corresponding to n and n_1 ,

$$i/i_1 = n/n_1 = e^{-\epsilon V_1/kT}$$
 (14)

This result may be obtained more directly by considering the equilibrium of electrons in an enclosure containing a rod of the metal in question whose sides are protected by an insulated covering, the ends only being free. The enclosure is divided into two halves by a semi-permeable membrane, which stops the gas but not the electrons, one of the two free ends being in each half of the chamber. The method which has been

adopted, however, brings out a number of additional relations and shows that the whole treatment is self-consistent. Since we know from experiment that i_1 is expressed accurately by $i_1 = AT^{\dagger} e^{-b/T}$ we have

$$i = AT^{\frac{1}{2}}e^{-(b+\phi)/T}, \tag{15}$$

where $\phi_i = \epsilon V_1/k$, is half the number of calories which are equivalent to the work $N \epsilon V_1$ if N is the number of molecules per gramme-molecule. In (15) A and b are constants, but ϕ_i , which is proportional to the change in the contact potential difference caused by the gas, may in general be a function of the temperature as well as of the pressure of the gas.

Suppose that in the region of temperature under consideration ϕ is represented by

$$\phi = \sum_{n=0}^{\infty} a_n T^n + \sum_{n=0}^{\infty} b_n T^{-n}, \tag{16}$$

where the coefficients are functions of the pressure of the gas, then

$$i = Ae^{-a_1}T_2^{\frac{1}{2}}e^{-(b+a_0)/T - \sum_{n=0}^{\infty} a_nT^{n-1} - \sum_{n=0}^{\infty} b_nT^{-n-1}}.$$
 (17)

But since i is still of the form $CT^{\frac{1}{2}}e^{-d/T}$, where C and d are constants, it follows that all the coefficients $a_2 \dots a_{\infty}$ and $b_1 \dots b_{\infty}$ are negligible; so that

$$\phi = a_0 + a_1 T. \tag{18}$$

If C and d denote the values of A and b when gas is present,

$$C = Ae^{-a_1}$$
 or $\log C - \log A = -a_1$, (19)

and
$$d = b + a_0$$
 or $d - b = a_0$. (20)

To satisfy the linear relation demanded by figs. 1 and 2 it is necessary that $-a_1/a_0$ should be a positive quantity which is independent of the pressure of the gas. If, as appears on the surface, this ratio is independent of the nature of the gas as well as the pressure, the generality of the constancy of $-a_1/a_0$ is still further extended; but it is possible that all the effects with a given metal which are apparently caused by various gases are really due to traces of some particular gas which is present as an impurity. This does not seem probable in the case of tungsten but it cannot be denied that it is possible. Thus a_0 and a_1 have opposite signs and for a given metal are in a constant ratio. This ratio is nearly the same, and may be exactly the same, for both metals. The values of $-a_1/a_0$ given by figs. 1 and 2 are: for tungsten, $4\cdot16\times10^{-4}$ and for platinum $4\cdot36\times10^{-4}$. If we denote the value of this ratio by α we may write equation (18)

$$\phi = \alpha_0 (1 - \alpha T). \tag{21}$$

For the temperatures at which the experiments have been made α T is less than 1 for both metals; so that the sign of ϕ is that of α_0 . For tungsten

 a_0 is positive; so that ϕ is positive at these temperatures, and the effect of the gaseous contamination should be to make the metal electronegative to pure tungsten. The actual change V_1 in the contact potential difference, compared with the pure metal, should be given by

$$V_1 = -\frac{k}{\epsilon} a_0 (1 - \alpha T) \times 300 \text{ volts.}$$
 (22)

The data taken from fig. 1 on substitution in the formula make the extreme value of V_1 at 2000° K., corresponding to $\log_{10} A = 29$ and $b = 11.5 \times 10^4$, equal to -0.87 volt. For platinum a_0 is negative; so that contamination with hydrogen should make the pure metal more electropositive, as is known to be the case. The magnitude of the change should be comparable with that for tungsten. The calculated contact potentials are those which would be observed at the high temperatures of the experiments; so that they are not strictly comparable with those given by experiments at ordinary temperatures.

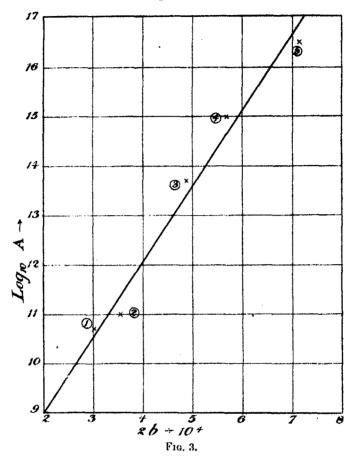
Emission of Positive Ions.

There is some evidence that the linear relation between the constants A and b in the emission temperature formula holds for the emission of positive ions as well as of electrons, although the data available in this case are much less The writer* has measured the values of A and b for the positive emission from an old platinum wire in the following gaseous atmospheres:-(1) Oxygen at 2 mm., (2) hydrogen at 1.9 mm., (3) air at 760 mm., (4) hydrogen at 226 mm. and (5) nitrogen at 2.8 mm. These appear to include all the known data. The values of log10A are plotted against the corresponding values of $2b op 10^4$ in fig. 3, the points being numbered in accordance with the foregoing enumeration. It seems hardly likely that the observed linearity is due to a coincidence, although there was evidence during the experiments with hydrogen that complete equilibrium between the metal and the gas was not attained. Thus too much reliance should not be placed on the points numbered (2) and (4). The whole question, of course, calls for further investigation. It is interesting to note that the value of α , or $-\alpha_1/\alpha_0$, is of the same order as that for the negative emission. Data taken from fig. 3 give

$$\alpha = 7.0 \times 10^{-4}$$

If the change in the negative emission constants is so intimately connected, with the contact difference of potential as we have supposed, one might

expect an effect of a similar order of magnitude on the positive emission, on a number of different views as to the precise nature of the latter.



Some General Considerations.

The matter which has been had under consideration suggests a number of interesting points which, unfortunately, can hardly be discussed with profit at present on account of the meagreness of the experimental data. It may, however, be permissible to point out that if the change in the emission constants for platinum which is caused by hydrogen is an effect of positive hydrogen ions present in the surface layer, it is equally likely that the contrary effect with tungsten in various gases is due to negative ions, originating from the gases, which are in a similar condition to the positive ions in the case of platinum. In any event it seems improbable that the effects are not attributable to a similar cause acting in opposite senses in the

case of these two metals. In this connection it is interesting to notice that the effect of hydrogen on the constant a_0 for the positive emission from platinum is opposite to that for the negative emission for this metal, and is in the same sense as that for the negative emission from tungsten. These differences are to be expected if it is a question of the sign of dissolved or adsorbed ions.

In concluding, the writer ventures to hope that the considerations which have been brought forward will help to introduce some degree of orderliness into the experimental values of the emission constants, which, it must be admitted, are at present somewhat incoherent.

General Equations for the Neutralisation of Dibasic Acids, and their Use to Calculate the Acidity of Dilute Carbonate Solutions.

By E. B. R. PRIDEAUX.

(Communicated by Prof. F. G. Donnan, F.R.S. Received May 26, 1915.)

The numerous equations which have been proposed to express the equilibrium of acids, bases, salts, and their ions are generally convenient to apply, since in each particular case different simplifying assumptions can be made. The subject has now reached a stage, however, at which these can be replaced by equations of a more general nature.

Practically the most important cases are those of the mono- and poly-basic acids combined with strong monacid bases, which furnish the bulk of those mixtures of balanced hydrion concentration which are used in physiological chemistry and also effect the physical regulation of the physiological fluids themselves.

The relation between the stage of neutralisation and the hydrion concentration of these acids is such that, usually, only two dissociation constants need to be considered. Thus the constants of a tribasic acid, such as orthophosphoric, are each one of a higher order of magnitude than that which precedes it, and at the stage of neutralisation at which the third constant begins to have an effect, that of the first is inappreciable. The general equation for a weak dibasic acid will alone be considered in what follows.

This will dissociate in the steps-

$$(H')(AH') = K_1(H_2A),$$

 $(H')(A'') = K_2(HA').$

The degrees of dissociation α_1 and α_2 may be defined as the ratio of the primary (HA') and secondary (A'') ion respectively, to the total acid in any form of combination, *i.e.* as ions, undissociated acid and undissociated salt. Hence (HA') = α_1 C, (A'') = α_2 C.

In the simplest possible case, the total concentration is such that the dissociation of all salts may be taken as unity. If at the same time the concentration is not so low that the production of the hydrion and hydroxylion necessary for the equilibria causes a rearrangement of a considerable fraction of the salt present; then it has been shown by Michaelis* that—

$$\alpha_1 = \frac{K_1(H^*)}{(H^*)^2 + K_1(H^*) + K_1K_2},$$

$$\alpha_2 = \frac{K_1K_2}{(H^*)^2 + K_1(H^*) + K_1K_2}.$$

If the total acid concentration is C, then the ionised part is α_1 C, etc., and the number of equivalents of ionised acid are equal to the added base.

Hence
$$\frac{\text{equivalents base}}{\text{mols, acid}} = R = \frac{A' + 2A''}{C} = \alpha_1 + 2\alpha_2$$

And the expression above may be transformed into

$$R = \frac{1}{1 + K_2/(H^{\cdot}) + (H^{\cdot})/K_1} + \frac{2}{1 + (H^{\cdot})/K_2 + (H^{\cdot})^2/K_1K_2}.$$
 (1)

This formula does not give quite accurate results when the total concentration is high, and especially at high alkalinities. It fails altogether at very low concentrations.

In order to include these cases also, an extension may be made of the method applied by the author to the correction of the third dissociation constant of orthophosphoric acid.

The ratio (R) of equivalents alkali to mols. of acid is equal to

$$\frac{(\text{NaHA}) + 2(\text{Na2A}) + (\text{NaOH})}{(\text{NaHA}) + (\text{Na2A}) + (\text{H2A})}.$$
 (2)

Also

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$$NaHA = (HA')/\alpha_1, \qquad (Na_2A) = (A'')/\alpha_2,$$

$$(\mathrm{NaOH}) = \frac{(\mathrm{OH'})}{\alpha_8} = \frac{\mathrm{K_w}}{(\mathrm{H'})\,\alpha_3},$$

in which α_1 , α_2 now stand for the fractions dissociated, not of the total acid, but of the primary and secondary salt.

By the help of these, and of the ionic equations

$$(H')(HA') = K_1(H_2A), \qquad (H')(A'') = K_2(HA'),$$

^{* &#}x27;Die Wasserstoffionen Konzentration,' p. 30.

all the terms of equation (1) above, except the third term of the numerator, may be transformed into terms containing either (NaHA) alone or (Na₂A) alone.

By the first method

$$R = \frac{(\text{NaHA}) + 2 \,\text{K}_2(\text{NaHA}) \,\alpha_1 / (\text{H}^*) \,\alpha_2 + \text{K}_w / (\text{H}^*) \,\alpha_3}{(\text{NaHA}) + \text{K}_2(\text{NaHA}) \,\alpha_1 / (\text{H}^*) \,\alpha_2 + (\text{H}^*)(\text{NaHA}) \,\alpha_1 / \text{K}_1}. \tag{2a}$$

By the second method

$$R = \frac{2 (\text{Na}_2 \text{A}) + (\text{H}^*) (\text{Na}_2 \text{A}) \alpha_2 / \text{K}_2 \alpha_1 + \text{K}_w / (\text{H}^*) \alpha_3}{(\text{Na}_2 \text{A}) + (\text{H}^*) (\text{Na}_2 \text{A}) \alpha_2 / \text{K}_2 \alpha_1 + (\text{H}^*)^2 (\text{Na}_2 \text{A}) \alpha_2 / \text{K}_1 \text{K}_2}.$$
 (2b)

Or dividing through by (NaHA), etc.,

$$R = \frac{1 + 2 K_2 \alpha_1 / (H^*) \alpha_2 + K_w / (H^*) (N_8 HA) \alpha_3}{1 + K_2 \alpha_1 / (H^*) \alpha_2 + (H^*) \alpha_1 / K_1},$$
 (3a)

or

$$R = \frac{2 + (H^{+}) \alpha_{2} / K_{2} \alpha_{1} + K_{w} / (H^{+}) (Na_{2}A) \alpha_{3}}{1 + (H^{+}) \alpha_{2} / K_{2} \alpha_{1} + (H^{+})^{2} \alpha_{2} / K_{1} K_{2}}.$$
 (3b)

If the third terms of the numerators are omitted, and the simplifying assumptions of p. 536 are introduced, it may easily be shown that either of these equations becomes identical with the transformed Michaelis' equation (1).

If the equations 3a and 3b are used as they stand, the former is suitable for solutions containing only small proportions of alkali, the latter for solutions containing small proportions of acid. The two give identical results for solutions containing moderate proportions both of HA' and of A''.

If the total concentration is moderate, (NaHA) and (Na₂A) in the third terms may be obtained with sufficient accuracy from the amounts of acid and alkali taken.

Dilute Solutions.—At higher dilutions, the hydrolysis appreciably affects the amounts of primary and secondary sult. The third terms of the numerators must then be expressed differently.

Let C. as before, be the total concentration of H₂A and its ions.

Then either A" or H₂A will be vanishingly small in comparison to the other two forms of combination.

Which form may be neglected is easily to be determined by means of the K_1 and K_2 equations on p. 536 combined with the value of (H^*) chosen.

In the more acid solutions

$$C = (HA') + (H_2A).$$

And, since ionisation is practically complete,

$$(NaHA) = (HA').$$

Or, substituting for H₂A its value $\frac{(H^*)(HA')}{K_1}$, it follows that $(HA') = (NaHA) = \frac{K_1C}{K_1 + (H^*)}.$

Similarly, it may be shown that in the more alkaline solutions

$$(A'') = (Na_2A) = \frac{K_2C}{K_2 + (H')}.$$

The complete equations for high dilutions become

$$R = \frac{1 + 2K_2/(H^*) + K_w \{K_1 + (H^*)\}/(H^*) K_1 C}{1 + K_2/(H^*) + (H^*)/K_1},$$
 (4a)

$$R = \frac{2 + (H^{*})/K_{2} + K_{w} \{K_{2} + (H^{*})\}/(H^{*}) K_{2}C}{1 + (H^{*})/K_{2} + (H^{*})^{2}/K_{1}K_{2}}.$$
 (4b)

These equations are the quantitative expression of the fact that extreme dilution increases the amount of alkali required to produce a given value of (OH'). The third term of the numerator is a measure of the extent to which the hydrion concentration of a given partly neutralised acid varies with the dilution.

Application to Carbonic Acid.—The carbonate equilibrium is the chief physical agent which regulates the hydrion concentration, not only of physiological fluids, but also of the hard waters, fresh and salt, the acidity of which has so intimate a connection with the growth of plaukton and other simple organisms. This acidity may in most cases be directly determined, but the determination is sometimes inconvenient.

In an important research, e.g. by Bronsted and Lund* on the physical and biological conditions of Danish lakes, the amount of CO₂ and of CaO has been determined in each case, but not the acidity of the water. The use of the equations will, it is hoped, enable the missing datum to be supplied in cases such as these.

The acidities of carbonic acid at different stages of neutralisation as determined by Auerbach and Pick† and others, may now be compared with those calculated by the different formulæ given above, using $K_1 = 3.04 \times 10^{-7}$, Walker and Cormack, and $K_2 = 6 \times 10^{-11}$, Shields, Koelichen, McCoy, Auerbach and Pick (*loc. cit.*).

Experimental Values at C = 0.2 mol. H_2CO_3 per litre.

^{* &#}x27;Chem. Phys. Untersuchungen der Dänischen Gewässer,' 1912.

^{† &#}x27;Arb. aus d. Kais. Gesundheitsamt,' vol. 38, (4), p. 562 (1912).

The first Table given below has been calculated from formulæ 3a and 3b, p. 537, using $a_1 = a_2 = 0.8$ and $a_3 = 0.9$ in a 0.1 molar solution. The second Table is from the simplified formula 1, p. 536. The two give almost identical results in the middle of the neutralisation curve at $(H^*) = 1 \times 10^{-10}$. But in the more alkaline solutions the introduction of the third term makes a considerable difference.

Thus by interpolation on the curves, $-\log(H^*) = 11.7$ from the general formula, and 12.3 from the simplified formula at R = 2. The former thus gives a better agreement with the experimental values of Auerbach (11.4 at $(Na_2CO_3) = 0.05$) than the latter.

0.75

1 .375

1 .86

1.98

1.99

Dilute Carbonate Solutions.—The calculation of the acidity of solutions, of which the total concentrations are lower than those of $CaCO_8$, etc., in presence of the specified amounts of H_2CO_3 , are, of course, equally applicable to carbonates of the calcium group as to those of the sodium group. There are a few experimental values of the (H^*) of hard waters which will serve to check the accuracy of the values in Tables III and IV, which are based on equations 4a and 4b.

0.60

0.03

().24

R

Table III. $C = 0.001 \text{ mol. } H_2CO_3 \text{ per litre.}$ $-\log{(H')} = (4.75)$ 5.00 6 .00 6 .70 7:00 8 .00 9.00 10 00 R = (0.00)0.03 0.23 0.60 0.75 0.975 1 '06 1 44 $-\log{(H')} = 10.50$ 11 .00 R 1 .86 2 .50 Table IV.

$$C = 0.0001.$$

$$-\log(H^{\circ}) = 5.26 \quad 5.50 \quad 6.00 \quad 6.70 \quad 7.00 \quad 8.00 \quad 9.00 \quad 10.00 \quad 10.50$$

$$R = 0.00 \quad 0.09 \quad 0.23 \quad 0.60 \quad 0.76 \quad 0.98 \quad 1.12 \quad 2.01 \quad 3.62$$

In a 0.001 molar solution of Na₂CO₃ Auerbach (*loc. cit.*) found $(OH') = 0.27 \times 10^{-3}$ $\therefore (H') = 2.37 \times 10^{-11}$, $-\log (H') = 10.63$.

The solubility of CaCO₃ (calcite) is, according to Schloesing* and Kohlrausch

* 'Comptes Rendus,' vols. 74, 75 and 90 (1872 and 1880).
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and Rose,* 0.13 mgrm. mols. per litre. McCoy and Smith estimate it as 0.166, and Kendal† as 0.1433 at 25°. McCoy and Smith‡ state that the alkalinity of this solution corresponds to $-\log{(H^*)} = 9.96$, while the interpolated value on the curve at C = 0.0001 is 10.1. This point is difficult to realise experimentally. Two determinations were made by the electrometric method of the hydrion concentration of water saturated with Iceland spar and decinormal with respect to NaCl or KCl.

First result (H') =
$$9.3 \times 10^{-11}$$
. Second result (H') = 4×10^{-10} .
 $-\log (H') = 10.03$, $-\log (H') = 9.40$.

The saturation was effected by a current of air free from CO₂ in the first case, by shaking in a silver bottle in the second case.

The experiments were made in the Muspratt Laboratory, Liverpool; the second in conjunction with Mr. J. Twomey.

The alkalinity of filtered CaCO₃ solution (without chloride) was also measured by the colorimetric method (using phenolphthalein), both in deep Nessler glasses and in a Donnan colorimeter. The comparison solution was an alkaline phosphate of which $(H') = 7.1 \times 10^{-10}$. The mean of five measurements gave for the carbonate solution $(H') = 4.3 \times 10^{-10}$.

An unsteadiness in the results is to be expected, both on account of the slowness of the heterogeneous equilibrium, and on account of the extreme sensitiveness of the alkalinity to traces of H₂CO₃ in this part of the curve, which is accentuated by the high dilution. A discrepancy between the observed and calculated alkalinities of sodium acetate has been accounted for by Walpole on similar grounds.§

The acid part of the curve may be tested by the help of the measurements of Walker and Kay. Waters of different "degrees of hardness" made from standard lime-water were brought into equilibrium with the CO₂ of the air, and the acidities were measured by a colorimetric method:—

Concentration of carbonate expressed as molecules CaCO _a .	· (H·).
0 ·O ₃ 5	1 × 10 ⁻⁸
0 ·O ₄ 5	1·1 × 10 ⁻⁷

^{* &#}x27;Zeitsch. f. phys. Chem.,' vols. 12, 44, 64 (1893-1903).

^{† &#}x27;J. Amer. Chem. Soc.,' vol. 33, p. 468 (1911).

[‡] 'Phil. Mag.,' I, p. 958 (1912).

^{§ &#}x27;Trans. Chem. Soc.,' vol. 105, pp. 2502, 2511 (1914).

^{|| &#}x27;J. Soc. Chem. Ind.,' vol. 31, p. 1014 (1912).

These figures suffice for a calculation of the degree of neutralisation R, for the total alkali (in equivalents) is 0.001 and 0.0001, and the same figure represents the bicarbonate ion concentration (HCO₃'), since it can be shown that the fraction of original HCO₃' forming H_2CO_3 is negligible at the hydrion and total concentrations given. The excess of carbonic acid, H_2CO_3 , should be that which is in equilibrium with the CO₂ pressure of the air, i.e. by Bohr and Bock's results 1.35×10^{-5} .

It may, however, be derived with more certainty from the constant of the homogeneous equilibrium

$$(\mathrm{H_2CO_3}) = \frac{(\mathrm{H}^*) \times (\mathrm{HCO_3}')}{\mathrm{K_1}}.$$

This gives in the first case

$$(H_2CO_3) = 3.29 \times 10^{-5}$$

and in the second case

$$(H_2CO_3) = 3.63 \times 10^{-5}$$
.

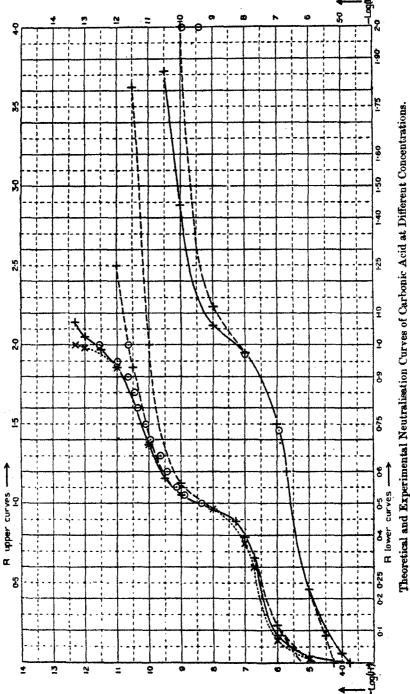
Introducing these values, the ratio R is found to be in the first case 0.97, and in the second case 0.73.

The values of the ratio from the general equation at the given acidities C = 0.001 and C = 0.0001, are 0.98 and 0.75 respectively.

If, however (H₂CO₃) is calculated from the absorption coefficient of the gas-liquid equilibrium as above, the calculated value of R in the second case falls right off the curve.

The observation that (H₂CO₃) calculated from the homogeneous is slightly greater than that calculated from the heterogeneous equilibrium has been made by several investigators and has not yet been adequately explained.

It is clear from all the evidence that has come under the author's view that the data of the heterogeneous equilibria, i.e. pressure of CO_2 and solubility of $CaCO_3$, can only be used with great caution to calculate (H') by means of the (H₂CO₃) and (CaCO₃) (solubility product) which are supposed to be in equilibrium with the gas and solid phase respectively. On the other hand, the analytical data, total concentration of H_2CO_3 and of alkali in a homogeneous solution, can be so used with considerable confidence. The easiest method of employing the equations is evidently to plot a section of the curve corresponding to the known carbonic acid concentration, choosing values of (H') above and below that which is to be expected. The ordinate from the value of R found then gives the correct figure.



Theoretical and Experimental Neutralisation Curves of Carbonic Acid at Different Concentrations.

NOTES ON DIAGRAM.

Ordinates = - log (H'). Left-hand numbers refer to upper curves, right-hand to lower.

Abscisse = ratio alkali to acid. Upper numbers refer to upper curves, lower numbers to lower curves.

Upper Curves.

- + + and plain line—values calculated by formulæ 3a and 3b at C = 0.1.
- × × and dotted line—values calculated by formula 1
- \bigcirc Auerbach's values at C = 0.2.
- ++ and broken line—values calculated by formulæ $\begin{cases} at C = 0.001 \text{ upper.} \\ at C = 0.000 \end{cases}$ lower.
- · Lower Curves-Dilute carbonate on larger scale.
 - + + and plain line—values at C = 0.001.
 - + + and broken line—values at C = 0.0001.

 - N.B.—'The third points in Tables I and II have been erroneously plotted as 0.17 and 0.14.

Volatilisation of Extremely Thin Radioactive Deposits.

By A. B. Wood, M.Sc., Oliver Lodge Fellow and Assistant Lecturer in Physics, University of Liverpool.

(Communicated by Prof. Sir E. Rutherford, F.R.S. Received July 1, 1915.)

Introduction.

Within the last few years papers dealing with the volatilisation of radioactive substances have been published by various authors. The principal aims of the experiments described in these papers may be classified under three heads:—

- (a) To determine the temperatures of volatilisation of the various members of the active deposits of radium, thorium, and actinium; in some cases with a view to the classification of these substances in the periodic system.
- (b) To prove that these extremely small quantities of matter form definite chemical compounds in a manner similar to that of the commoner elements.
 - (c) To separate the various members of the series from one another.

Other interesting results, which throw light on the phenomena of volatilisation, have also been reported, but these have always formed a subsidiary part of the researches described. Makower* determined the

* Makewer, 'Manch. Lit. and Phil. Soc.,' vol. 53, Part II (1909), and 'Le Radium,' vol. 6, p. 50 (1909).

temperatures of volatilisation of radium A, radium B, and radium C, in air, and showed that the effects observed depended to some extent on the nature of the surface on which these substances were deposited.

Schrader, working with the active deposits of actinium and thorium, found that volatilisation commenced at a much lower temperature if the platinum wire coated with the active deposit were first exposed to an atmosphere of chlorine. He also put forward the view that, in consequence of the production of ozone by the α -particles, oxides are formed of the components of the active deposit. This explanation cleared up the mystery with regard to the great divergence between the results obtained by Russell[†] and those of Makower, previously mentioned.

Results of a similar character have also been described by Barratt and Wood,‡ and more recently by the author.§

These authors have also shown the possibility of separating radioactive substances which have not yet been separated by other methods.

One feature, common to all the experiments mentioned, is the reference to possible sources of error in the determination of volatilisation temperatures. Hence it appeared to the author that an investigation of a few of the most important factors which may influence the volatilisation of these exceedingly thin films was desirable.

It is necessary, in an investigation of the nature just mentioned, to choose some substance whose behaviour when heated to various high temperatures is fairly simple. In addition to this, the behaviour of this substance must be typical of the other substances of the same character. Barratt and Wood, in studying the volatilisation of thorium B and thorium C, showed that the curve connecting the amount volatilised with temperature was quite simple in the case of thorium B, whereas the curve for thorium C was more complex. The author has also shown that the volatilisation curve for thorium D is similar to that for thorium B. We may thus reasonably assume that the volatilisation curve of thorium B is typical of that for any single constituent in the active deposits of radium, thorium, or actinium.

Consequently thorium B is the substance employed in the present experiments for an investigation of the various influences which affect the volatilisation of the active deposits.

^{*} Schrader, 'Phil. Mag.,' vol. \$4, p. 125 (1912).

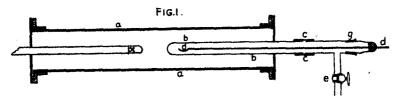
[†] Russell, 'Phil. Mag.,' vol. 24, p. 134 (1912).

¹ Barratt and Wood, 'Phys. Soc. Proc.,' vol. 26, pp. 248-260 (June, 1914).

[§] A. B. Wood, 'Phil. Mag.,' vol. 28, pp. 808-818 (December, 1914).

Apparatus and Experimental Procedure.

The apparatus employed is shown diagrammatically in fig. 1. An electric furnace, whose temperature could be measured accurately by means of a platinum thermometer and Callendar-Griffiths bridge, was used to heat the active material. The furnace and thermometer have been described in detail in a previous paper.*



aa. Porcelain lining of furnace.

pt. Platinum thermometer.

bb. Fused silica tube.

dd. Light nickel spoon.

e. Tap connecting to pump and pressure gauge.

Temperatures above 1100° C, were estimated by extrapolation of the curve connecting temperature and current through the furnace. The active substance was placed inside a tube of fused silica, closed at one end, arranged centrally in the furnace and symmetrically with regard to the platinum thermometer (see fig. 1). By means of a long nickel spoon, fixed to a ground glass joint which closed the cold end of the tube, the active material could be introduced or removed quickly from the silica tube. The nickel spoon was of very small heat capacity, and attained the temperature of the furnace in a very short time. This point is of importance, and will be referred to later (see Section 3). The silica tube was connected by means of a side tube to a vacuum pump and pressure gauge, thus making it possible to heat the active substance at any desired pressure. This arrangement also proved extremely useful in evacuating the tube between successive experiments, in order to remove any volatilised active material which would necessarily be A strongly emanating source of radio-thorium present in the tube. (equivalent in activity to 1 mgrm. of radium bromide) was used as a supply of active deposit. By a simple arrangement this could be obtained on one side only of the plate exposed to the emanation, and by varying the conditions of exposure a considerable range of activity could be obtained. In all experiments, except a few of those described in Section 2, exposures were made without electric field, a thin layer of tissue paper separating the radio-thorium from the metal foil, so that the possibility of thorium X being deposited on the foil was reduced to a minimum. The active deposit obtained in this way decayed accurately with a period of 106 hours, thus proving it to be free from thorium X. All measurements of activity were made by α -rays, an electroscope of the Rutherford pattern being used for this purpose.

Before commencing to take activity measurements, the active deposit was allowed several hours (generally overnight) to attain equilibrium. The following procedure was adopted in the determination of the percentage of thorium B volatilised. Equilibrium having been attained, several readings of the activity were taken and the mean time of observation noted. The deposit was then placed in the nickel spoon and introduced into the furnace for the desired interval. When a period of not less than six hours had elapsed after the removal of the active deposit from the furnace, the a-activity was again measured and at the end of this time the unvolatilised portion of the deposit had again attained equilibrium. From the observed and calculated values of the activity at the time of the second set of measurements the percentage volatilised is easily deduced. At the end of every experiment similar to the one just outlined, the silica tube was evacuated to a pressure of about 2 cm. of mercury in order to free it as far as possible from the volatilised portion of the active deposit.

Factors Influencing Volatilisation.

Earlier experiments have shown that the volatilisation of a thin film of radioactive matter varies enormously with the conditions to which it is exposed. For example, the kind of surface on which the film is deposited has a marked effect, whilst several experimenters have recorded notable variations with different gases on the furnace tube. It is unnecessary at this stage to enter into a discussion of numerous other sources of influence on this phenomenon, but the following list will serve as a guide to some of the principal factors which have been investigated in detail. The effects of variation on the following conditions have been studied:—

- 1. Nature of the surface on which the active substance is deposited.
- 2. Thickness of the layer of active material.
- 3. Period of heating.
- 4. Temperature.
- 5. Pressure of the surrounding gas.
- 6. Nature of the surrounding gas.

The first five of these factors will be considered in the order given above. The consideration of the sixth, i.e. the influence of the nature of the gas surrounding the active material, will be discussed in a later communication.

^{*} See paper by Barratt and Wood, loc. cit.

1. Influence of Surface.—Before investigating the other factors which may influence the volatilisation of the thorium B, it is necessary to choose a suitable surface as a "support" or "base" for the deposit. Barratt and cood showed the necessity for a perfectly clean surface, since a thin film of grease, or other substance which easily volatilises, will carry away the active material with it. It is essential then to use some substance as "base" which can be cleaned easily and thoroughly, either by heating or by treatment with acids. Platinum and quartz are both ideal in these respects. It is interesting, however, to examine other substances as to their suitability. Substances whose melting points are below 1000° C, can at once be dismissed; again, all substances the volatilisation of which is detectable below this temperature are unsuitable.*

Makower in his work on the volatilisation of radium C from surfaces of nickel, platinum, and quartz has shown that volatilisation of the active substance is appreciable in all cases between 700° and 800° C. radium C was driven off nickel and platinum at 1200° C. but not from the quartz till a temperature of 1300° C. was reached. Barratt and Wood, using thorium active deposit, confirmed this observation of Makower that the initial temperature of volatilisation was the same whether the active substance was deposited on quartz or platinum; but found it impossible to volatilise the whole of the deposit from either quartz or platinum even after prolonged heating at 1300° C. These conclusions are strongly supported by the results It was found that after heating the active of the present experiments. deposit on platinum for 10 minutes at a white heat (temperature estimated at 1600° C.) in the blowpipe flame there still remains an appreciable amount of thorium B unvolatilised. A similar result was obtained when quartz was used as the base. With regard to this unvolatilised portion of thorium B, the following experiment is instructive. A platinum foil coated with thorium active deposit was heated for about 60 minutes at 1200° C. and approximately 99 per cent, of the thorium B volatilised. The portion remaining on the platinum foil, i.c. the 1 per cent., was allowed to attain equilibrium, when it was again heated for the same time at 1200° C. It was found now that only 18 per cent. of this remaining portion of the original deposit was volatilised. These observations seem to indicate that a certain fraction of the molecules of the active deposit are held to the surface of the platinum by forces of cohesion due to the molecules of platinum in their immediate neighbourhood. Possibly this small percentage of the active deposit has penetrated below the

^{*} A list of elements with their melting points, boiling points, and temperatures of initial volatilisation is given in a table in Kaye's 'X-rays.'

[†] Makower, 'Manch. Lit. and Phil. Soc.,' vol. 53, Part II (1909).

surface molecules of the platinum by the process of radioactive recoil. Thus, when exposing the platinum plate to the emanation, an atom of thorium A on expelling an α -particle might, by its energy of recoil, travel a distance equal to the depth of several layers of molecules below the platinum surface. This recoiling atom of thorium B disintegrates (with emission of a soft β -ray) into thorium C without appreciably changing its position; then, when the atom of thorium C expels an α -particle, the recoiling atom might either penetrate still further into the platinum or make its escape again from the surface. Another possible explanation of the phenomenon is that the molecules of the active deposit and platinum conceivably intermingle near the surface on account of the energy of heat motion at these high temperatures.

Recent work by Roberts* has shown that platinum, or one of its oxides, is volatilised at temperatures between 1000° C. and 1200° C., hence it is quite probable that a small portion of the active deposit is carried off by this means, in addition to the normal volatilisation.

When the active material was heated on a nickel surface, the effects observed were very conflicting. The temperature at which volatilisation commenced agreed fairly well with the temperatures noted when platinum and quartz surfaces were used. At higher temperatures, however, large divergences were sometimes observed—the results seeming to depend on the condition of the nickel surface before exposure to the emanation. Thus it was noticed that the results were more consistent when the nickel surface, before exposure to the emanation, was oxidised by heating strongly in a blowpipe flame.

The following shows the result of a series of experiments using nickel and platinum surfaces:—

Surface.	Time of heating.	Percentage thorium C remaining.	Percentage thorium B remaining.	
Platinum Nickel (polished)		8 8 4	1 8·5	

(1) First Heating at 1200° C.

After equilibrium had again been attained, the foils were reheated.

^{*} Roberts, 'Phil. Mag.,' 6, vol. 25, p. 270 (February, 1913).

Surface.	Time of heating.	Percentage remaining thorium C (i.e., thorium C left from (1)).	Percentage remaining thorium B (i.e. thorium B left from (1)).
Platinum	min. 60 60	82 89	70 76

(2) Second Heating at 1200° C.

A third heating in the blowpipe flame (temperature between 1500° C. and 1600° C.) showed that there was a large percentage of the active deposit left from (2), still unvolatilised. It will be clear from these results that it is with only very great difficulty that the last 2 or 3 per cent of the active deposit can be volatilised. Again, it is more difficult to remove the active deposit from nickel than from platinum. As one would expect, the nickel, on removal from the furnace at these high temperatures, is always coated with a thin film of black oxide, which renders this substance unsuitable as a base for several reasons—in particular, the complication of the α -ray measurements due to the absorption in the oxide film. Again, volatilisation of this film night introduce serious errors in the measurements. A surface of iron or steel is objectionable for similar reasons.

Using copper and brass surfaces this trouble of oxidation was still further increased, the comparatively low melting point of copper (1084° C.) being another serious objection to its use at high temperatures.

The metals osmium, iridium, and tungsten would be excellent for the purpose, since volatilisation of these elements has not been detected below 1400° C. in vacuo—on account of their expensive nature, however, they were not used in the investigation.

From the above considerations it is clear that platinum and quartz are the most suitable materials to employ in a research of this kind. On account of the ease with which it can be cleaned and manipulated platinum has been used as base for the active substance in all the experiments subsequently described.

2. Density of the Deposit.—When referring to such minute quantities of substance as the active deposits from the various radioactive emanations we cannot use strictly the term "thickness." Assuming a uniform distribution of particles, a simple calculation of the thickness of a very active layer of thorium active deposit, equivalent in γ -activity to 7.5 mgrm. of radium per square centimetre of platinum, shows that only one thousandth of the platinum surface is covered by a layer one molecule deep, i.e. for every

thousand surface molecules of the platinum there is only one molecule of active deposit. Hence it seems advisable to use the term "density of the deposit" where density indicates the number of molecules of active deposit per unit area of surface. It will be at once clear that this term is used in a relative sense; thus when one layer of active deposit is said to be ten times the density of another, a comparison is made between the number of molecules per square centimetre in the two cases.

It is well known that in the case of volatilisation of metals such as iron, gold, or platinum, the amount volatilised is proportional to the time of heating and to the surface area exposed. This is far from being the case, however, in the volatilisation of minute quantities of matter such as we are now considering. It will be shown later that the amount volatilised is not a linear function of the time of heating.

There are two methods open to us for varying the density of the deposit: (a) by varying the time of exposure to the emanation, without employing an electric field; (b) by exposing for different times with an electric field.

- (a) By comparing the γ -activity of the active deposit with that of a standard source of radium, a simple calculation gives us the approximate number of active deposit molecules per square centimetre. Variations of exposure from 1 to 40 hours have been made without electric field, representing a range of density from 1.5×10^{10} to 1.5×10^{11} active deposit molecules per square centimetre—the number of platinum molecules in a surface layer being of the order 10^{14} . No regular variations in the amount volatilised with change of density of the deposit were observed, all differences being well within the experimental error. Hence, under these conditions, the volatilisation is independent of the time of exposure to the emanation.
- (b) If an electric field is used when exposing to the emanation, the density of the deposit can be increased to about one hundred times the maximum possible by method (a), i.e. to a density of about 10^{13} molecules per square centimetre.

Now, however, fairly large and almost unaccountable variations occur. Several explanations of these variations can be suggested. They may be due (1) to the collection of charged dust particles or other nuclei, coated with active deposit, (2) to the formation of charged aggregates of active deposit, and to the non-uniformity of the layer of active deposit collected by this method, as compared with that obtained by the ordinary process of diffusion. In all cases, however, the amount volatilised from a plate exposed, till equilibrium is reached, by method (b) is greater for short periods of heating than that volatilised from a plate exposed by method (a).

This gives strong support to the view that dust particles or other nuclei coated with the active deposit have been collected on the plate by the electric field used in (b)—consequently, when such a plate is introduced into the furnace, the dust burns rapidly, and carries away the active deposit with it. This question will be discussed later (see Section 3). The following Table gives a comparison of a series of results obtained by the two methods just outlined:—

	Percentage thorium B volatilised at 795° C.			
Time of heating.		to emanation without ic field.	Exposure to emunation with electric field.	
	2 hours' exposure.	40 hours' exposure.	24 hours' exposure.	
min.		1		
5	82	27	52	
15	60	58	81	
30	78	81	86	
60	88	87	90	

The above remarks must be modified, of course, when we are considering the volatilisation of the portion which remains after the platinum and active deposit have been once heated to temperatures over 1000° C.—this has been explained in Section 1. For experiments of this character the results are always the same, whatever the density of the original deposit.

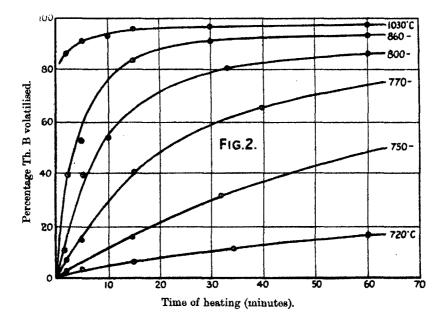
It appears, then, that the most consistent results are obtained when the platinum foil is exposed to the emanation without electric field, the volatilisation in that case being practically independent of the time of exposure. In all subsequent experiments the active deposit was collected by exposure to the emanation for six hours without electric field.

3. Variation of Period of Heating.—A point of great importance in the study of the problem of volatilisation is to determine the rate at which the active material is removed from the surface.

The experimental procedure was as follows: After the furnace had attained a steady state (usually after about 2 hours' preliminary heating) the active deposit, previously measured, was introduced into the furnace for a definite period, by means of the nickel spoon. On removal its activity was measured as explained above. The silica tube was then evacuated to remove volatilised active deposit, and a second source of active deposit introduced for another different period. This process was repeated until a series of observations had been made giving the relation between the time of

heating and the amount volatilised at a particular temperature. The temperature of the furnace was now altered to another value, and, after a steady state had again been reached, the above order of experiment repeated. It should be pointed out at this stage that the minimum time of heating in the furnace was about two minutes, on account of the small but appreciable time (perhaps 30 seconds) required by the nickel spoon to attain the furnace temperature. This difficulty was surmounted, as far as seemed possible, by lining the spoon with a thin layer of asbestos, consequently the small piece of thin platinum foil would probably reach the furnace temperature in a much shorter time than that required for the spoon.

The result of such a series of observations is shown in fig. 2.



Two prominent features of these curves will be noticed at once.

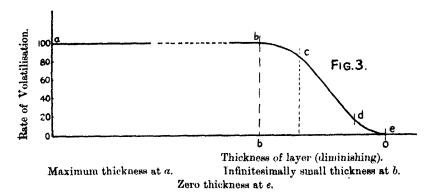
- (1) The amount volatilised increases at first rapidly, then more and more slowly as heating is continued, *i.e.* the rate of volatilisation decreases rapidly with time of heating, particularly at high temperatures.
- (2) The initial rate of volatilisation increases very rapidly with small increases of temperature. This point is shown more clearly in fig. 4, which will be discussed in Section 4.

Another, though perhaps less important, feature of these curves will be noticed from a consideration of the rate when a large percentage has been volatilised. A decided flattening of the curves becomes evident as the

amount volatilised approaches the maximum value, thus indicating that it would take an extremely long period of heating to remove the last traces of the thorium B—in fact, a similar curve (not shown in figure) at 1200° C. runs practically parallel to the time axis, with 99 per cent, as ordinate. This gives further confirmation of the results mentioned in Section 1.

The first explanation of the form of the curves which suggests itself is that they are exponential. It seems quite reasonable to suppose that the rate of volatilisation is proportional to the amount of active substance present on the platinum foil at any particular time, i.e. when we are dealing, as in this case, with a comparatively small number of molecules. The facts do not support this view, however, and it becomes necessary to look for some other explanation. Of course, it is quite probable that several factors are involved in the complex behaviour of the active deposit; hence a consideration of the following hypothetical case may throw some light on the problem.

Suppose we could obtain on a platinum surface a layer of active deposit of measurable thickness (say 0.001 mm.). Let us consider what happens when this layer is heated. Up to a certain critical point, b in fig. 3, one



would expect the rate of volatilisation to be constant, i.e. the amount volatilised is proportional to the time of heating, but when the depth of the layer had decreased to one or two molecules the rate of volatilisation would begin to decrease, at first slowly, then more rapidly, until only those molecules of the active deposit which are intermingled with the platinum molecules are left. At this stage, d in fig. 3, the rate of volatilisation decreases more slowly, since the remaining molecules are subject to a different law of force—the cohesion of the platinum molecules—from that of the active deposit molecules volatilised in the earlier stages. Fig. 3 is a diagrammatic representation of the process just outlined The latter portion

of the curve, between the points c and e, represents the result of an actual experiment similar to the one described at the beginning of this section.

As was made clear in Section 2, the thickness of the active deposits is always less than that at the critical stage b—consequently the rate of volatilisation is never constant initially. If the above suggestions are correct we should expect, on investigating very thick layers of active deposit, to include more and more of that portion of the curve lying between the points b and c. Unfortunately, we have no sources of thorium emanation at present available, from which we can collect such thick layers of active deposit by diffusion. Owing to the disturbing action of dust particles, when an electric field is used to increase the density of the deposit, the results obtained in such cases cannot legitimately be compared with those obtained by the diffusion method used in the above experiments.

We now come to the second and, perhaps, more important feature of the curves shown in fig. 2, viz. the influence of temperature on the rate of volatilisation. The problem bears a close similarity to that of the emission of ions from a hot metal. Thus if we assume that the volatilised particles behave like a perfect gas, the calculation of the rate of volatilisation is analogous in practically all respects to that in the case just mentioned. Regarding the steady state as the result of a dynamical equilibrium between the molecules going from the layer of active deposit to the air and those going from the air to the deposit, we obtain the well-known relation connecting the rate with the absolute temperature T

$$Rate = AT^{\dagger}e^{-B/T}, \tag{1}$$

where A and B are constants which can be determined experimentally.

The expression for the rate, just given, was first deduced by Richardson in his researches on emission of ions from hot bodies, and was subject to the condition that the number of free electrons per unit volume of the metal is independent of the temperature. He has since modified his views by assuming that the number of free electrons in the metal is proportional to T^i , whence

$$Rate = AT^2e^{-\frac{1}{2}T}.$$
 (2)

The assumption just mentioned was made in order to explain the observed values of the specific heat of electricity. More recently Richardson† has given another deduction of the second formula based on the quantum theory.

^{*} Richardson, 'Phil. Mag.,' vol. 23, p. 604 (1912).

[†] Richardson, 'Phil. Mag.,' vol. 28, p. 633 (1914).

Planck* also has obtained the relation $AT^2e^{-B/T}$ by consideration of the vapour pressure of a solid at very low temperatures, using the assumption that the entropy of the solid at these temperature will be practically independent of the temperature, while that of the vapour can be considered like that of a perfect gas.

It seems very doubtful, however, whether the assumptions used by Planck will apply to the case under consideration, i.e. to the evaporation of a metal at high temperatures. In this case, a lower power of the factor T would be expected.

Both the relations just given require that the rate should be constant when the temperature is constant, but, as we have already seen, this is far from being the case, the rate varying considerably with the amount of material volatilised.

Consequently we must introduce a factor $\phi(N)$ into the expression for the rate, in order to make this quantity in agreement with observations—the function $\phi(N)$ expressing the rate as a function of the number N of thorium B molecules volatilised. We now have

Rate =
$$AT^*e^{-B/T}\phi(N)$$
, (3)

where $n = \frac{1}{2}$ or 2.

The form of the function $\phi(N)$ has already been discussed from the physical standpoint, hence we need only concern ourselves with a consideration of the remaining factor. From observations of the initial rate of volatilisation at two different temperatures the values of A and B in equation (2) can be calculated, and the rates at any other temperatures deduced. The following Table provides a comparison between the observed and calculated values of the initial rates at different temperatures.

Absolute temperature T.	Observed rate.	Calculated rate, using relation ATle-B/T.	Calculated rate from
803	<0.01	Extremely small	Extremely small
998	0 ·5	0.53	0.20
*1081	1 .4	1.4	1.4
1063	8 .4	3 61	8.4
*1108	8.0	8.0	8.0
1139	20	23 -8	16
1803	Very great	980	880

^{*} The observed rates at these temperatures were used in the calculation of the constants A and B in the expressions for the rate.

^{*} Max Planck, "Die gegenwärtige Bedeutung der Quantenhypothese für die kinetische Gastheorie," 'Vorträge über die kinetische Theorie der Materie und der Electricität — Mathematische Vorlesungen au der Universität Göttingen,' VI.

Considering the extreme sensibility of the expressions AT'e-B/T and AT²e^{-B/T} to small changes of temperature, the agreement between observed and calculated values is good. It will be noticed, however, that the factor To or To has practically no effect on the value of the expression for the rate until the temperature reaches a high value—thus both expressions for the initial rate of volatilisation agree equally well. It is only possible, experimentally, to distinguish between the two forms when the temperature is in the neighbourhood of 1000° C.; unfortunately at this temperature it is practically impossible to measure the initial rate. Similar results are found if, instead of using the initial rates, we consider the rates of volatilisation at a later stage of the process. Thus the rates of volatilisation at different temperatures when 40 per cent. of the active material has been removed are in the same relative proportion as the initial rates at the same temperatures. This only holds, however, up to a point where about 80 or 90 per cent. of the thorium B is volatilised. Beyond this point, the whole process is changed on account of the effects previously discussed.

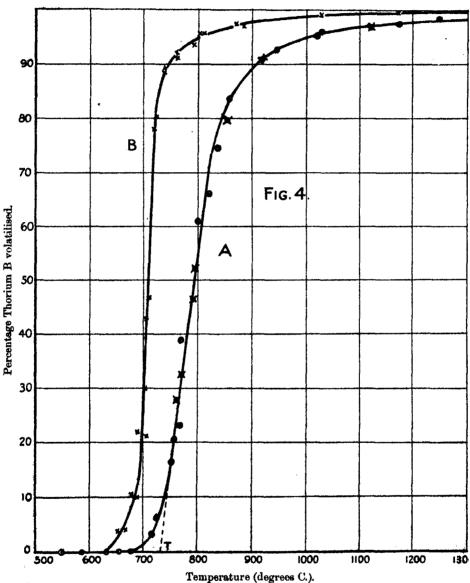
The results of the experiments on the rate of volatilisation of the active deposit thus seem to support the view that the volatilisation proceeds on similar lines to the emission of ions (positive or negative) from a heated metal. Other experimenters have shown* that there is a close similarity between the laws of disintegration of a heated wire and the leak of positive electricity from it. The present experiments support this view, although the only safe conclusion which can be given at present is that the formula for the volatilisation—besides containing terms varying more slowly—may be expected to contain the factor $e^{-B/T}$ or $e^{-Q/RT}$, where R is the gas constant and Q the latent heat of vaporisation: this result, of course, is well-known from ordinary thermodynamical considerations.

4. Variation of the Temperature.—From the point of view of interest this factor should have been considered earlier, but for several reasons it seemed advisable to defer it until the questions raised in Section 3 had been discussed. Barratt and Wood (loc. cit.) investigated the question by heating thorium active deposit for a constant time (15 minutes) at various accurately measured temperatures. Their work led to a result 750° C. as the temperature of volatilisation of thorium B. In the present experiments the procedure adopted was exactly the same—the constant period of heating in this case again being 15 minutes.

Curve A, fig. 4, is a combination of the results obtained in the present work with those obtained in a previous research by Barratt and the author. The observations made in the present research are indicated in the figure by

^{*} See J. J. Thomson's 'Conduction of Electricity through Gases,' p. 213, Chap. VIII.

a circle—those in previous work by Barratt and Wood by a combination of a circle and a cross. It will be seen that the two sets of observations are in excellent agreement. One important difference, however, should be noted.



Curve A. At 760 mm. pressure.
Curve B. At 3 mm. pressure.

××× © © Present paper.

© Ø Barratt and Wood.

The temperature of volatilisation, as given by Barratt and Wood, was "slightly lower than 750° C."—it is evident from the figure that if the main portion of the curve is produced to cut the axis at T, the temperature obtained, 740° C., agrees very well with the value just given. This temperature, 740° C., is that at which the thorium B begins to volatilise very rapidly. Below this temperature, however, a small amount of volatilisation is observed, but this quickly falls to a quantity too small for detection at about 680° C. Of course, the lowest temperature at which it is possible to detect volatilisation is even lower than this, but in that case the time of heating must be considerably increased. The following observations at temperatures below 680° will illustrate this point:—

Temperature.	Percentage thorium B volatilised on heating.		
Tomporavuro.	(1) 15 minutes.	(2) 60 minutes.	(8) 5 hours.
° С. ӨЗО 550	0	1	3 1

The form of the curve A, fig. 4, is interesting. It will be noticed that the amount volatilised increases at first slowly, then much more rapidly as the temperature increases. When a fairly large percentage has been removed, however, the rate of volatilisation rapidly falls off with further heating at higher temperatures. Of course, a series of curves similar to the one just described could be constructed from fig. 2 directly.

If the form of the function ϕ (N) in equation (3), Section 3, were accurately known it would be possible to calculate the total amount volatilised in a given time at any desired temperature.

5. Variation of Pressure of the Surrounding Gas.—All the experiments described up to this stage have been carried out with the air at atmospheric pressure in the silica tube. We shall now consider the effects observed when the active deposit was heated at pressures considerably lower than this. After its α-activity had been measured the active deposit on the platinum foil was placed on the nickel spoon and introduced into the silica tube. The air in the tube was immediately expanded into a bottle of large volume previously exhausted to the required pressure. Hence it was possible to obtain almost instantaneously any desired pressure in the tube by arranging that the volume of the receiver was very large compared with the volume of the silica tube. A series of observations of this kind, keeping

the time of heating constant (15 minutes), was made at different temperatures and pressures.

The result of such a series of observations at a pressure of 3 mm, is shown in curve B, fig. 4. Comparing the two curves A and B it is evident that the process of volatilisation takes place on very much the same lines in each case. Thus the slow initial rise, followed by the much steeper portion and ended by another slow increase, is characteristic of both curves. In the "low pressure" curve, however, the central portion is considerably steeper than the corresponding portion of the "atmospheric pressure" curve, indicating that volatilisation is much more rapid in the former case. Another difference between the two curves is the lowering (about 50° C.) of the initial temperature of volatilisation at low pressures. It should be noticed, too, that at low pressures it is still found practically impossible to volatilise the last traces of the active deposit.

The following Table gives a few of the results of a series of experiments carried out on the variation of the amount volatilised at different temperatures, the pressures varying from 760 mm. to 3 mm. of mercury:—

	Percentage volatilised. Pressure, cm. of mercury.			
Temperature.				
	76 app.	15.	1 .5.	0.3.
°C. 710 757 800 1030 1175	4 18 45 95 97	18 47 73 —	60 83 93 98 5	67 92 96 90 99

Summary.

The more important factors which influence the volatilisation of extremely thin films of the radioactive deposits have been investigated experimentally. Each of these sources of influence has been considered separately by eliminating, as far as possible, the disturbing effects of the others. Thorium B, for reasons given in the earlier part of the paper, has been chosen as typical of all similar constituents of the active deposits of radium, thorium, and actinium.

560 Volatilisation of Extremely Thin Radioactive Deposits.

The influence of the following factors on the process of volatilisation has been examined:—

- (1) The surface on which the active substance is deposited.
- (2) Variation of the "amount per square centimetre" of the active deposit collected on the surface.
- (3) Variation of the period of heating. Curves connecting "percentage volatilised" with "time of heating" at a series of different temperatures are given.
 - (4) Variation of temperature—the time of heating remaining constant.
 - (5) Variation of the pressure of the surrounding gas.

It has been shown to be extremely difficult to remove, by heating alone, the last traces of the active deposit from surfaces of quartz, nickel, or platinum. A suggested explanation of this is given and verified experimentally. The most consistent results are obtained when the surface is exposed to the emanation without electric field, in which case the volatilisation is independent of the time of exposure to the emanation. The volatilisation is shown to obey practically the same law as the rate of emission of positive ions from a hot body, this expression—Rate = $AT^n e^{-B/T}$ —being modified by the introduction of a factor $\phi(N)$ which depends on the amount of active deposit which has been volatilised. The function $\phi(N)$ is considered from a physical standpoint, the mathematical relation being extremely complex.

A comparison of the volatilisation curves at pressures of 760 mm. and 3 mm. is given, a lowering of the initial temperature of volatilisation at low pressure being observed. The volatilisation curve at atmospheric pressure agrees extremely well with that given in a previous paper by Barratt and Wood (loc. cit.).

In conclusion, I should like to express my warmest thanks to Prof. L. R. Wilberforce for his interest and encouragement, and to Prof. Sir E. Rutherford and Dr. N. Bohr for kind help and criticism.

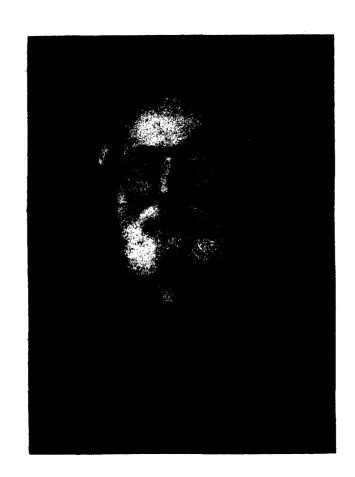
OBITUARY NOTICES

OF

FELLOWS DECEASED.

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REV. ROBERT HARLEY, M.A., F.R.S.

ROBERT HARLEY, 1828-1910.

THE Harleys can be traced back to a Norse stock of Harlas. Harley's family was settled in Dunfermline for hundreds of years. His father, Robert Harley of Dunfermline, began life as a merchant with property bequeathed to him by his uncle, Sir William Mitchell (a Vice-Admiral who fought with Nelson), but he gave up a good business in Scotland to become a Wesleyan minister in England. His mother was Mary Stevenson, niece They were living at Seacombe, near of General Stevenson of Ayr. Liverpool, when Robert Harley was born (January 23, 1828). small boy he was devoted to swimming but found arithmetic the most He was in this respect very backward, but seems irksome of his studies. suddenly to have developed talent and enthusiasm while at school at Blackburn, which led to his accepting a post as mathematical master at a Seacombe school when he was only 16. Shortly after this he was attracted by the mathematical problems which were appearing in 'The Lady's and Gentleman's Diary.' His interest in the solutions had one very important result, for it brought him into contact with a young barrister, nine years his senior—James Cockle—who later became a distinguished mathematician, a knight, a Fellow of the Royal Society, and Chief Justice of Queensland. They became life-long friends, and there is no doubt that his scientific work was more influenced by Sir James Cockle than by any other single individual who could be named. When Sir James died in 1895 Mr. Harley wrote the obituary notice for the Royal Society's 'Proceedings.' At the age of 17 he returned, as head assistant-master, to his old school at Blackburn. This was kept by William Hoole, J.P., a well-remembered mayor of the town, by whom Viscount Morley of Blackburn and many others who have since risen to distinction were educated.

At the age of 23 he determined to be a minister, and became a divinity student at Airedale College, Bradford, and on completing his course accepted a call to become minister of the Independent Chapel at Brighouse, in the West Riding of Yorkshire. When he was 26 he married Sara Shoyan, niece of Mr. Hoole, and daughter of James Shoyan of Wigan, also of Scottish extraction, and lived happily with her for fifty-one years. served at Brighouse for fourteen years. His four children, two sons and two daughters, were all born there. His congregation built him a comfortable manse and a much larger chapel. He laboured strenuously for the good of the growing village, preaching in the open air with his friend William Booth, afterwards famous as the Father of the Salvation Army. He started Penny Readings for the poor, and himself took part in them every Saturday He was much beloved by the people, and Harley Street, Harley Court and Harley Place remain to link his memory with the new prosperous town. During the last four years of his Pastorate at Brighouse he was VOL, XCL-A

Professor of Mathematics and Logic at his old college, Airedale (now the United College), Bradford. During this time George Boole was a frequent Mr. Harley was devoted to him, and was captivated visitor at the Manse. by his application of mathematics to logic. He became, perhaps, the most notable of Boole's admirers and followers, and after his death in 1864 frequently lectured on "George Boole and his Laws of Thought." In 1868 he went to be the pastor of the oldest Congregational church in (Bond Street) Leicester. He was there four years, and took a very active part in the life of the town. He served on the Executive Committee of the National Education League, an office which brought him into association with the Right Hon. Joseph Chamberlain, for whom he entertained a high regard. He was elected a member of the first Leicester School Board; he helped to establish the School of Art; was an active member of the Free Library Committee; was honorary Curator of the Museum, and President of the Literary and Philosophical Society. In the latter capacity he introduced to a Leicester audience as lecturers many of the foremost scientific men of the day, including Huxley, Tyndall and Spottiswoode. He himself lectured on "The Moon," "Meteoric Showers," and many other subjects.

In the summer of 1872 he visited Mill Hill with the object of entering his eldest son at the now well-known school. The Head Master—R. F. Weymouth—was so impressed with his energy and capacity that he offered there and then to create for him a position as Vice Master. This was accepted, and Mr. Harley moved from Leicester and built for himself a house—Burton Bank, Mill Hill—which became the first boarding house in connection with the School. The house speedily filled, and for nearly ten years he was Vice Master of Mill Hill and Minister of the Chapel. Through his efforts the school swimming bath was built, the playing fields improved, and a record in the number of boys established.

Apart from the School he interested himself in the life of the village. He erected a lecture hall, which was opened by his friend the late Earl Stanhope, and made a centre of instruction and entertainment. In 1882 Mr. Harley returned to Yorkshire as Principal of Huddersfield College, which post he filled with marked success until 1886, when he accepted a call to the principal Congregational church in Oxford. Soon after his arrival the University of Oxford conferred upon him the degree of M.A. (honoris causa), on which occasion the Public Orator paid a graceful tribute to his labours in the cause of religion and philanthropy as well as to his attainments as a mathematician. He took a leading part in founding the Oxford Mathematical Society, and, in 1889, lectured before the Ashmolean Society on "George Boole and his Logical Method."

He was compelled to take a rest in 1890, and, at the instance of a Special Committee of the Congregational Union of England and Wales, he accepted a cabled invitation to take temporary charge of the Mother Congregational Church of New South Wales (Pitt Street, Sydney). He stipulated beforehand for two months, but he remained for eight months and was

invited to stay on permanently, but he had left his wife and daughters in England and had no wish to settle down in the Antipodes. He made a host of friends in Australia, and lectured before the Royal Society of New South Wales and Queensland, the Union of Sydney University, and many other bodies.

On his return to England he, in 1892, went once more back to Yorkshire, this time as Minister of Heath Church, Halifax. In 1895 he retired and bought a house at Forest Hill, S.E., where he lived quietly and happily for the remaining fifteen years of his life. He preached and lectured frequently, and advocated total abstinence incessantly. He was, in fact, one of the pioneers of the Temperance movement. At the British Association he often presided at the Temperance breakfast. He was a Vice-President of the National Temperance League for thirty-three years, and only a few weeks before he died a reception was given in his honour by a number of workers interested in temperance, at the Memorial Hall, Farringdon Street, presided over by Sir John Thomas. On this occasion he gave an address, entitled "Reminiscences of an Octogenarian—Chiefly Temperance." was over 82 he spoke with much energy and stirring elequence, exhibiting an intellectual vigour in his old age which amazed his friends.

He was always a keen student of astronomy, and was a Fellow of the Royal Astronomical Society. He had an observatory built in his garden for a fine telescope which was presented to him by personal friends.

He was a friend of Herschell, Airy, Huggins, Ball, and other well known astronomers. On one occasion he visited Lord Rosse at Parsonstown.

He was a Life Member of the British Association, and acted as Secretary of Section A in 1868 (Norwich), and in 1871 (Edinburgh). He was Vice-President in 1873 (Bradford), 1888 (Bath), and 1891 (Cardiff).

Throughout his life Mr. Harley found recreation in mathematical investi-These may be said to have commenced with his friendship with His earliest paper was published in 1851, and bore the Sir James Cockle. title "Impossible Equations." A few years later he became engaged on the problem of the finite solution of the general equation of the fifth degree, which had occupied the minds of the most celebrated analysts of the 18th and 19th centuries. He and Cockle were in almost daily correspondence for several years, particularly 1858 to 1862, on the subject. He approached the problem by seeking to determine in an explicit form a certain sextic equation-termed a resolvent-on the solution of which that of the general quintic may be made to depend. It appeared subsequently that Jacobi earlier, and Malfatti even earlier still, had expounded the doctrine of sextic resolvents, but, notwithstanding, much merit remained in the work, for it was independent and lucid. In particular he devised a new cyclical symbol and a new cyclical function which much simplified and facilitated laborious calculations. He later extended his researches on the theory of equations far beyond the limits at first proposed. His results were published in the 'Manchester Memoirs,' the 'Quarterly Journal of

Mathematics,' the 'Proceedings of the London Mathematical Society,' and in the 'Philosophical Transactions of the Royal Society of London.' Brioschi, the well known mathematician of Italy, wrote a paper which showed the relation of some work of Malfatti to that of Harley and Cockle. Cayley was from the first interested in the work, and made additions in his own masterly style. He supported Harley's candidature for the Royal Society, and he was elected a Fellow in 1863. 'His claims for the distinction were set forth in the following terms:—"The discoverer of the new cyclical process and other improved methods of mathematical analysis; the author of several papers....' On Impossible Equations,' On the Method of Symmetric Products,' On the Theory of Quintics,'' On Certain Circular Functions,'' Researches on the Theory of the Transcendental Solutions of Algebraic Equations,'' Among those who supported his candidature were Cayley, Sylvester, Hirst, H. J. S. Smith, Boole and Spottiswoode.

Following these investigations Harley next took up the subject of differential equations, and with the collaboration of R. Rawson and Cockle constructed a theory of "Differential Resolvents." Cockle encountered a class of differential invariants which he named "Criticoids." examined by Harley in a masterly manner. Harley's friendship with Boole now had a determining effect upon the trend of his mathematical thought. By studying Harley's results Boole was led to a discovery in the Theory of Differential Equations, which Harley subsequently generalised. paper ever published by Boole was on this subject ('Phil. Trans.'), and contains a résumé of Harley's researches down to that date. On Boole's death the Editor of the 'British Quarterly Review' applied to Harley to prepare an essay on Boole's life and writings. This was willingly undertaken, and an elaborate article appeared in the July number of the Review for 1866. He received much help from Spottiswoode (later President of the Royal Society), who invited him to London that he might have ready access to the British Museum, the Royal Society, and other libraries. The obituary notice of Boole for the 'Proceedings of the Royal Society' was also written He expounded Boole's logical method before the British Association in 1886 (Nottingham) and in 1870 (Liverpool). He wrote and lectured on the subjects of the "Laws of Thought," and occupied himself with the study of earlier efforts to facilitate the processes of formal logic by the use of mathematical operations. He spent some time at Chevening, Sevenoaks, the residence of Lord Stanhope, studying the papers and inventions (including two calculating machines) of Charles, third Earl Stanhope, F.R.S. (elected in 1772 at the age of 19). In 1879 he wrote in the April number of 'Mind' an article about the Stanhope Demonstrator for performing logical operations; in his will he bequeathed to the Ashmolean Museum the Stanhope Demonstrator and the Stanhope Arithmetical Machine (dated 1780), both of which had been presented to him by Arthur Philip, fifth Earl Stanhope (ob. 1905). On his retirement he still pursued his mathematical studies, but he never lived to complete the 'Treatise on Quintics' which he had begun. He sat for some years on the Council of the London Mathematical Society, of which he was a member for forty-five years. When over 80 he would come in every day from Forest Hill to spend his time in the library of the Athenseum Club, of which he was a member for a long period.

He preached on Sunday, July 17, 1910, with no premonition that it was to be his last sermon. He went off to Cromer for a holiday but had to be brought back to his home on Monday, July 25; he passed away peacefully the next day, July 26, 1910. He was buried in Ladywell Cemetery. The Rev. Sylvester Horne, M.P. for Ipswich, and Chairman of the Congregational Union of England and Wales, delivered a memorial address in which he dwelt on his "lovable and striking personality"; he also read a letter from Sir James Murray to his daughter, in which was said:—

"Your father had a very wide circle of friends; very few men ever had so many. In the religious world, in the world of science, in the total abstinence movement and in the sphere of national politics he was widely known and as widely held in esteem. His annual visit to his beloved Yorkshire to preach Sunday School sermons was almost like a triumphal progress as friends gathered from far and near to hear and see him Politicians will remember him as an unflinching friend of liberty and equality of opportunity, of unsectarian education and social progress, a man of supreme moral courage who was never afraid to be on the side which was for the moment that of the minority. He lived a full and an honoured life."

It may be added that Mr. Harley's life was also happy. He and Mrs. Harley celebrated their golden wedding at Forest Hill in 1904, when all their four children were seated round the dinner-table. For fifty years they had been spared a single bereavement; but the next year the eldest daughter died, and within a few weeks Mrs. Harley followed her.

He was a man of overflowing spirits and merry conversation, and was able to a remarkable degree to inspire confidence and win affection. He was always a delightful person to meet. Those who knew him were impressed with the beauty of his disposition. He showed the kindest and most generous appreciation of the work of others. If there was a nice thing to be said the opportunity was not missed. He was one of the most remarkable and most versatile men which the Congregational Ministry has ever produced.

P. A. M.

JULES HENRI POINCARÉ, 1854-1912.

JULES HENRI POINCARÉ* was born at Nancy, April 29, 1854. His father was a medical man who is spoken of as enjoying, in an especial degree, the respect of his fellow-townsmen. His uncle was the father of the President of the French Republic. The boy was at the Lycée at Nancy from October, 1862, until August, 1873, leaving with the Prix d'Honneur au Concours Général en Mathématiques Spéciales. At the age of five he had suffered from a severe illness, and is described as a delicate boy, preferring the society of his sister to the games of his schoolmates. But any tendency to devote himself too exclusively to a contemplative view of life must, one feels, have received a rude shock from the experience which came to him at the age of sixteen. Nancy is about thirty miles south of Metz; his father was called upon in 1870, as a medical man, to help with the wounded, and the young Poincaré attended him as secretary. So anxious was he to read the only newspapers that were obtainable that he learned to read German for the purpose, so it is said. In later life he was one of the closest ties between the mathematical world of Germany and that of France.

In 1873 he was first among candidates for the Ecole Polytechnique at Leaving this in October, 1875, for the School of Mines, he was thence transferred as Engineer to Vesoul, about 80 miles south of Nancy, from April to December, 1879. During this year, in August, 1879, he became Doctor of Mathematical Science in the University of Paris. In December of the same year he was in charge of the Cours d'Analyse à la Faculté des Sciences de Caen. In Merch, 1881, at the age of nearly twentyseven, he was honourably mentioned as a competitor for the Grand Prix des Sciences Mathématiques awarded by the Academy of Sciences of Paris. In October, 1881, he became Maître de Conférences d'Analyse à la Faculté des Sciences de l'Université de Paris. In 1886 he was Professeur de Physique Mathématique et de Calcul des Probabilités at the University of Paris, and in 1896 Professeur d'Astronomie Mathématique et de Mécanique Céleste. He was chosen Member of the Academy of Sciences in the Section of Geometry in January, 1887, served as President in 1906, and was elected to the French Academy in 1908. He became a Foreign Member of the Royal Society in 1894, and on the inauguration of the Sylvester Medal for Mathematics in 1901, he received the first award. He died at his house in Paris in July, 1912, during the celebration by the Royal Society of its fifth jubilee. At the funeral ceremony the Society was represented by the Senior Secretary and the Astronomer Royal.

Such, in briefest outline, are the facts of his public career. To give any

^{*} A fairly complete bibliography, with a portrait and various appreciations, is edited by Ernest Lebon (Gauthier Villars, July 1, 1909). To this the writer is much indebted for dates and references.

complete account of his work is a task well nigh impossible on account of its vast range. His writings deal with nearly every branch of analysis, with every part of theoretical astronomy, and with most of the issues of modern mathematical physics. To whatever he deals with he brings a breadth of outlook, a wide generality of conception, which stirs the imagination, though it may puzzle the mind. Of the final value of his applications of mathematics to physics, time will pronounce; of the importance of the influence which his wide knowledge enabled him to exert, especially in his own country, there can be no question.

His contributions to pure analysis may be classed under differential equations, automorphic functions, general theory of functions, Abelian functions. Analysis Situs, arithmetic. The work on differential equations includes studies in extension of the general existence theorems given by Cauchy, and consideration, on the lines of Riemann and Fuchs, of the theory of linear differential equations. Also a systematic consideration of the utility, as solutions of differential equations, of series which are divergent, and yet asymptotic; this last, forced upon Poincaré's attention, presumably, by his astronomical studies, has had a wide development. It is, however, the general consideration of an infinite discontinuous group, in connection with which he refers explicitly to Fuchs, and the associated automorphic functions, which are the best known results of his study of differential equations. Historically an automorphic function arises among the formulæ for elliptic functions which are found in Jacobi's 'Fundamenta Nova.' Jacobi obtains a series whereby the square of the modulus, k^2 , can be expressed as a single-valued function of the ratio K'/K of the two so-called quarter periods. These are solutions of a linear differential equation of the second order whose independent variable is k^2 . Putting $\zeta = K'/K$, and $k^2 = \phi(\zeta)$, it is then natural to consider values of ζ of the form $\zeta'' = (a\zeta + b)/(c\zeta + d)$, in which a, b, c, d are constants. More simply and precisely, the facts are thus: Let 2\omega, 2\omega' be two arbitrary quantities whose ratio $\tau = \omega'/\omega$ is not real, but has its imaginary part positive. Let p(u) be Weierstrass's doubly periodic function with these quantities as fundamental periods. Then the function which is the ratio of $2p(\omega') + p(\omega)$ to $p(\omega') - p(\omega)$ is evidently a single-valued function of τ . It is in fact unaltered by substituting in it, in place of τ , the quantity $\tau + 2$; or by substituting $\tau/(2\tau+1)$; or more generally by replacing τ by $(p\tau + q)/(r\tau + s)$ in which p, q, r, s are any integers of which q and r are even, such that ps - qr = 1, so that p and s are odd. There is an infinite number of substitutions of this form: any two of them performed in succession give rise to a substitution of the same form, so that the aggregate of them constitutes a group of substitutions. Starting from an arbitrary value of T, whose imaginary part is positive, all the values of τ arising by these substitutions have their imaginary part positive; representing such values of τ on the upper half of a plane, in the usual way, a fundamental region of this half-plane can be named which is analogous to the fundamental

parallelogram used in the discussion of doubly periodic functions. Namely, every point of the upper half-plane which does not lie in this fundamental region can be obtained from one, and only one, point of this region by one, and only one, substitution of the group above described. If $\tau = \rho + i\sigma$, we may take for such a fundamental region the part lying between the lines $\rho = \pm 1$ and above the semicircles $(\rho \pm \frac{1}{2})^2 + \sigma^2 = \frac{1}{4}$, $\sigma > 0$. Poincaré's aim was to study the general properties of such infinite groups of (fractional) linear substitutions, and to obtain single-valued functions of the independent variable unaltered when this variable undergoes any substitution of the group. In both respects he obtained a brilliant success. It is not easy in a few sentences to give an account of his general theory of the groups; but it may be possible to make clear the way in which he constructs functions unaltered by a given group. Let

$$\zeta' = \vartheta_r(\zeta) = (a_r \zeta + b_r)/(c_r \zeta + d_r)$$

be any one of the substitutions of this group, the constants being chosen so that $a_r d_r - b_r c_r = 1$. Denote the denominator $c_r \zeta + d_r$ by $\Delta_r(\zeta)$. Let $H(\zeta)$ be a rational function of ζ , and μ_r a constant such that $\mu_{re} = \mu_{er} = \mu_r \mu_e$; let m be an integer. Consider the sum

$$\Theta(\zeta) = \sum_{r} \mu_r^{-1} H\left[\vartheta_r(\zeta)\right] \cdot \left[\Delta_r(\zeta)\right]^{-m},$$

which is to contain a term corresponding to every substitution of the group. It is then easy to prove that if for ζ we substitute $\vartheta_*(\zeta)$, any one of the transformations of ζ arising in the group, we obtain

$$\Theta\left[\vartheta_s(\zeta)\right] = \mu_s [\Delta_s(\zeta)]^m \cdot \Theta(\zeta).$$

The proof requires the assumption that the original series converges irrespective of the order in which the terms are taken; when we consider the generality of the ideas involved, Poincaré's proof that this may be so for proper values of m is one of the most striking portions of the work. Taking now another such sum as $\Theta(\zeta)$, having, however, in place of $H(\zeta)$ a rational function $K(\zeta)$, we shall have a similar equation. Thus the quotient of the two functions $\Theta(\zeta)$ is unaltered when the independent variable ζ is changed by any substitution of the group.

But now arises another consideration. Reverting to the function before considered,

$$\lambda(\tau) = [2p(\omega') + p(\omega)]/[p(\omega') - p(\omega)],$$

for purposes of illustration, we may regard τ , or ω'/ω , as the quotient of two independent solutions of a linear differential equation of the second order whose independent variable is λ . This is, in fact, a hypergeometric equation with singular points only at $\lambda = 0$, $\lambda = 1$, $\lambda = \infty$. If we have any function of the unrestricted complex variable λ , of which every existing branch is expressible, in the neighbourhood of any value λ_0 other than $\lambda_0 = 0$, or 1, or ∞ , as a power series in $\lambda - \lambda_0$, then it can be proved that, by regarding λ as that function of the new independent variable τ which is

given by the function above, the function under consideration becomes a single-valued function of τ . A particular case of this result is that the dependent variable of any hypergeometric differential equation is a singlevalued function of τ , if the independent variable be identified with $\lambda(\tau)$. These are evidently results of wide scope. Quite early (in 1883) Poincaré formulated a demonstration that every analytical function, $w = \phi(z)$, of an independent variable z, is such that both w and z may be regarded as singlevalued functions of an independent variable ζ . And both Klein (in 1882) and he (in 1883) have sought to make it clear that any rational algebraic equation f(y, x) = 0, connecting x and y, can be satisfied by regarding x and y as single-valued functions of another variable ζ , the suggestion of particular cases being that the functions can be taken to be automorphic functions in the sense already explained. To enunciate such a theorem, even though its exhaustive proof is a matter for subsequent investigation as it was in this case, may be to exert a great stimulus to the development of a theory. It ought, however, perhaps, to be mentioned that unless the equation f(y, x) = 0 is capable of being satisfied by rational functions, or by elliptic functions, of a parameter, the functions x, y of the new parameter, which are contemplated by the theorem, must possess an infinite number of essential singularities. The deductions to be drawn from the result must then, it would seem, be of a general character, and independent of the precise form of the functions. Poincaré himself returned to the matter in a paper on the uniformisation of analytic functions as late as 1907 (Acta Math., vol. 31), and the proof of the theorem has called forth an extensive literature. There is one matter of subsidiary importance to which a word may be given in connection with Poincaré's theory of automorphic functions. The division of the upper half of the plane of the complex variable into regions corresponding to the substitutions of a group may be made, as it was in the particular case previously taken for illustration, by means of circles having their centres on the real axis. Such circles have obviously at least some of the properties of straight lines in a plane; two such circles intersect in one point (in the upper half-plane); one such circle can be drawn through two given points. As straight lines are the curves which render the integral [ds stationary, taken between two given points, where $ds = (dx^2 + dy^2)^2$, so the circles in question are the curves which render the integral [ds/y stationary, y being the ordinate to the real axis and x the abscissa parallel to this axis. The relations of these circles are, in fact, those of the so-called straight lines in the geometry of Lobatchewski, the integral (ds/y), which we may call the separation of its two extreme points, replacing the distance of the Euclidian geometry. Similarly the integral $\int dx \, dy/y^2$, which we may call the extent of the region over which it is taken, may be used instead of the area. Every one of these elements, the circles with centres on the real axis. the separation, and the extent is unaltered by transformations

in which a, b, c, d are real, just as straight lines, lengths and areas are unaltered by movements in Euclidian geometry. It is thus convenient to make use of these elements in discussing the groups of such linear substitutions. It is in this sense that Poincaré employed non-Euclidian geometry in his discussion of these substitutions.

In addition to the systematic development of the theory of automorphic functions, of which we have given some account, Poincaré wrote several papers dealing with questions of Abelian functions. One of the briefest is an application of Kronecker's theory of characteristics to determine the number of pairs of variables for which two theta functions of two variables have each assigned values. The same theory is used also by Poincaré in his great paper on the equilibrium of a rotating fluid mass (Acta Math., vol. 7, p. 268, 1885-6). In Kronecker's hands the theory becomes an extension of Cauchy's theorem for integrals of functions of one complex variable to integrals of functions of several complex variables, and is put into connection with the theory of potential in any number of dimensions. It is interesting, then, to find papers of Poincaré dealing with extensions of Cauchy's theorem to functions of several complex variables, to see the theory of potential in any number of dimensions applied to the theory of integral functions of several variables, and to note how extensive and persistent were Poincaré's attempts to grapple with the problems of Analysis Situs in higher space. One of the problems to which Weierstrass devoted much consideration was to generalise the expression, as a quotient of two integral functions, of a single-valued analytic function of one variable whose only finite singularities are poles. Consider a single-valued analytic function of two variables; assume that about every finite pair of values of these the function is expressible, generally as a power series, but, if not, then as a quotient of two power series, with presumably only a limited range of The question is whether there exist two power series, each convergent for all finite values of the variables, as the quotient of which the function can be represented for all values of the variables. A difficulty arises from the fact that there are points at which the function has no definite value at all, the expressions which represent it having different limits according to the path by which the variables approach the pointit is desirable that the representation of the function as the quotient of two integral functions should be such that these integral functions do not simultaneously vanish except at points for which the function is actually indeterminate. Poincaré's papers in regard to the connection of the theory of potential with the theory of integral functions furnish a proof that such a representation is possible, and give rise incidentally to a splendid generalisation of Weierstrass's factor expression for an integral function of one variable. The real part of the logarithm of the primary factor $(1-z/c)e^{\psi}$, wherein ψ , which is introduced for convergence, may, for the purposes of our statement, be left out of account, is the logarithmic potential of a mass at the point c. We may thus say that, save for a correction

necessary to secure convergence, the real part of the logarithm of the integral function is built up from the potential of masses situated at the zero points of the integral function. When we come to an integral function of two variables, its zero points form a continuum. The integral expressing the potential of this continuum is the guiding portion of the real part of the logarithm of the integral function. The application of this suggestion to Weierstrass's problem requires the establishment of the notion of a definite continuum upon which the given function vanishes, and of another continuum upon which the function becomes infinite, and so furnishes a further incitement to the study of hyperspace. The ideas of which we have attempted to give some account are applicable to another pair of connected problems. One striking result of the manifold study of Abelian functions in the nineteenth century was the emergence of certain integral functions of several variables, known as theta functions, and, intimately connected therewith, of simultaneously periodic functions. A function of n variables u_1, \ldots, u_n may be such that if appropriate constants $\omega_1, \ldots, \omega_n$ be simultaneously added to the variables $u_1, ..., u_n$ respectively, the value of the function is unaltered. And there may be 2n sets of quantities such as $\omega_1, \ldots, \omega_n$ for which this is true. The theta functions are not so periodic; they are integral functions say of u_1, \ldots, u_n , associated with 2n sets of constants such as $\omega_1, \ldots, \omega_n$, so that for the values $u_1 + \omega_1, \ldots, u_n + \omega_n$ the function is multiplied by the exponential of a linear function like $\mathbf{A}_1 u_1 + \ldots + \mathbf{A}_n u_n + \mathbf{B}$.

For the theta functions and for the multiply periodic functions which can be formed from them, the $2n^2$ quantities such as $\omega_1, \ldots, \omega_n$ are connected together by certain bilinear relations of equality and inequality. The question then arises whether these relations are necessary for every possible multiply periodic function, and, a connected enquiry, whether the most general periodic function is expressible by theta functions. Even though, as is now the case, these questions have been given affirmative answers, there remains a need of some comprehensive and direct method of arriving at the result. And the suggestion that this will be associated with some greater insight into the possibilities of Analysis Situs (in space of 2n real dimensions) seems inevitable. Various lines of enquiry are thus opened; there is evidence that Poincaré gave attention to many of these. With Picard he published a note dealing with the bilinear relations among the periods of a multiply periodic function; to the properties of integral functions whose second logarithmic differential coefficients are periodic functions, and to the problem of sets of n integrals whose periods are expressible linearly by less than 2n sets, he devoted a long paper. To his study of the Analysis Situs in any number of dimensions several laborious memoirs bear witness. The surface imagined by Riemann. it is well known, serves the purpose of representing an algebraic function which is capable of several, say of n, values, as a single-valued function of position upon an n-sheeted surface. When, however, we seek to apply Cauchy's contour integral theorem to integrals of algebraic functions

considered on this surface, we are at once met by the fact that it is in general possible to draw closed curves upon the surface which are not capable of being continuously deformed to evanescence, and do not form the complete boundary of any portion of the surface. Such a circumstance arises also, evidently, for many surfaces; as for instance for the surface of an anchor ring. The question arises for such a surface, what is the least number of irreducible closed curves by means of which all others can be represented. In the case of a surface utilised in Riemann's manner for the representation of an algebraic function, the number so arising has the greatest importance for the theory, and is the most fundamental of the characters used to discriminate between algebraic functions of different individualities. When we pass from a surface of two dimensions to a closed space of n dimensions, and therein consider closed spaces of r dimensions, there is a similar question. Let two such closed spaces of order r be regarded as equivalent when either can be continuously deformed. into the other within the given space of n dimensions; there will be a least number, k, of closed spaces of order r in terms of which every other such space can be represented in the form

$$\mathbf{P} \equiv m_1 \mathbf{P}_1 + \ldots + m_k \mathbf{P}_k$$

wherein m_1, \ldots, m_k are integers. And there will be such a number k for each value of r which is less than n. These so-called numbers of Betti are in fact. equal in pairs, the number k for any r being equal to the number k for r' = n - r. This theorem requires, evidently enough, much greater precision in defining the meaning of equivalence than we can attempt here. For instance in the closed three-dimensional space interior to an anchor ring, every closed curve is clearly representable in terms of one such curve (unless itself deformable to evanescence); and every closed surface in this three-dimensional space, if not itself deformable to evanescence, is deformable to one surface, whose shape is that of an anchor ring interior to the given anchor ring, so that the two numbers of Betti are each equal to unity. It is obvious that two spaces which are capable of being put into point to point correspondence with one another must have the same numbers of Betti. Conversely, however, it was shown by Poincaré that the equalities of these numbers are not the only descriptive similarities necessary in order that two spaces should be capable of such correspondence.

The theory just referred to is suggested by the discussion of Riemann's surface. Riemann's own theory of the functions arising for such a surface was based upon a theorem of existence of potential functions, for which the evidence was, in the light of subsequent scrutiny, undoubtedly insufficient. The theorem in question, for which the physical suggestion is extremely cogent, has thence become the centre of a wide literature. To this also Poincaré contributed, with an extensive paper expounding a method of his own, in addition to which he wrote long papers dealing in general with the differential equations of mathematical physics.

In this survey we have left aside many of Poincaré's discoveries, for

instance, his brilliant additions to Laguerre's theory of the class of integral functions, or to Weierstrass's theory of monogenic functions. We have expounded instead some matters wherein is well seen the great generality and abstractness of much of his work. If his writings had been limited to his contributions to theory of functions, they would have left an enduring mark. We pass, however, now to consider in a few lines his extensive publications in the field of Astronomy and Dynamics.

As has been said, Poincaré was Professor of Astronomy from 1896, and, in addition to pure mathematics, he was probably interested from the first also in physical questions. As early as 1881, while yet Ingénieur des Mines, in 'Liouville's Journal' (vol. 7, p. 376), in a "Mémoire sur les Courbes Définies par une Équation Différentielle," we find the words:-"Prenons pour exemple le problème des trois corps; ne peut on pas se demander si l'un des corps restera toujours dans une certaine région du ciel." These words would seem to give the key to Poincaré's work in Astronomy and Dynamies; to ascertain whether the theory leads us to expect stability of motion and periodical recurrence of position may be said to have been his constant preoccupation. The publication of G. W. Hill's 'Researches in the Lunar Theory,' in America, in 1877-8, seems to have greatly impressed him. In vol. 1 of the Bulletin Astronomique (1884) he published a paper, "Sur Certaines Solutions Particulières du Problème des Trois Corps," which generalised Hill's idea of a periodic orbit for the Moon. And in the Preface to vol. 1 (1892) of his 'Méthodes Nouvelles de la Mécanique Céleste, speaking of Hill's contributions to the theory, he says: "Dans cette œuvre . . . il est permis d'apercevoir le germe de la plupart des progrès que la science a fait depuis." Many of the leading ideas of his theory of orbits were expounded in his essay "Sur le Problème des Trois Corps et les Équations de la Dynamique," which This was finished obtained the prize offered by the King of Sweden. in 1888, and published in revised form in 1890. In addition to this are to be mentioned the 'Méthodes Nouvelles,' already referred to (vol. 1, 1892; vol. 2, 1894; vol. 3, 1899), and the Sorbonne Lectures on Celestial Mechanics (vol. 1, 1905; vol. 2, 1907-9).

The dominating idea of the work is the possibility of the existence of solutions of theoretical exactness and of periodic character. In the case of the Earth and Sun and Moon, regarding the Sun as moving with constant angular velocity in a circle about the Earth and the Moon as moving in the same plane, G. W. Hill obtained, by actual computation, an orbit of the Moon relatively to the uniformly rotating line joining the Earth to the Sun, which is both re-entrant and symmetrical. Poincaré obtains a generalisation of this for any dynamical system in which the differential equations have an appropriate form, of wide generality, by reasoning which is quite general and quite simple; but this reasoning requires an appreciation of Cauchy's theorems of existence for the solutions of differential equations; and it is a characteristic property of the series which express the periodic solutions that

they converge. From the periodic orbit of the Moon Hill obtained, by variation of the equations, an equation for the motion of the Moon's perigee. In order to calculate the frequency of its oscillations without solving the equation, he introduced the use of determinants of indefinitely great order. That Poincaré should investigate the convergence of the method, and so set up a new engine of analysis, as an incident to his astronomical work, is characteristic of him. He further considers in much detail the general method of variation and the quantities which generalise the frequency considered by Hill, and their expansion as power series, as part of his theory of characteristic exponents. In another direction, also, he adopts the idea, suggested by Hill, of making the periodic solution the centre of the theory, by considering solutions which coincide with the periodic solutions after an infinite time, or did so coincide an infinite time before These are the so-called asymptotic solutions. periodic solutions and the asymptotic solutions are particular solutions of the equations, not containing the full number of arbitrary constants. Whereas the former converge, the latter, when expanded in terms of the small quantities, do not; they are, however, definitely and formally shown to be capable of use for approximations, in the manner of Stirling's series for the gamma function. The interplay between the original equations and the equations deduced by variation is again exemplified in Poincaré's consideration of integral invariants. In the motion of an incompressible fluid the integral which expresses the volume of any portion of the fluid is unaltered by the motion, if always taken over the same particles of the fluid. He obtains other integrals having the same property, and considers their relations in many aspects. That a quantity should contain in its expression a term of the form $t\cos(mt+h)$ is rendered by him as a statement that the quantity, though not remaining for all time of limited magnitude, does yet return infinitely often to within arbitrary nearness of its original value. This becomes a text for the consideration of dynamical systems with such a property—stable à la Poisson. In particular, a proof is given, as illustrating the theory of integral invariants, that for incompressible fluid in a closed vessel, if we consider the particles occupying at any instant a particular small volume, these particles (speaking generally) return infinitely often to this volume. This theory of integral invariants reappears in Poincaré's recent paper (Journ. de Physique, January, 1912). written in support of Planck's Theory of Quanta.

But it is impossible not to consider the relation of Poincaré's periodic solutions with the expansions used by practical astronomers, and a large part of his writing deals with this matter. Series had gradually been introduced containing only sines and cosines—that is terms $A\cos(nt+h)$, but no terms such as $t\cos(nt+h)$, or such as t^k , in which the time occurs outside the periodic functions—the evident intention being to obtain series which might serve to express the circumstances for all time. Apparently the possibility of such series may have been recognised d'Alembert.

(cf. E. W. Brown, 'Lunar Theory,' p. 239). Poincaré attributes the series to Newcomb ('Smithsonian Contributions to Knowledge,' December, 1874), who used them for the motion of the planets, and after him to Lindstedt. For the case of the Moon Delaunay's series are to be referred to Poincaré investigates Lindstedt's series again, and extends their scope; but he proves that they are not as a rule convergent. His method of proof is extremely simple, if not wholly convincing for all possible cases. It may be said to be part of his theory of periodic solutions. It is related also to his general theorem as to the existence of uniform integrals of the astronomical equations. He proves, however, that the Lindstedt series are asymptotic, in the sense in which Stirling's series for the gamma function are asymptotic; they give a rule for writing down a finite number of terms approximating very closely to the functions sought, but the approximation cannot be made arbitrarily close. To the consideration of these series and the related investigations of Delaunay, of Bohlin, and of Gyldén, a large part of the second volume of the 'Méthodes Nouvelles' is devoted. Sorbonne lectures a different plan of exposition is followed. Lagrange's method of successive approximation is first used to obtain expansions wherein the time occurs explicitly outside the periodic functions. A proof is then given that the terms in which the time enters in this way may be absorbed; for if they be omitted they can be re-found from the terms which remain, by a change of variables and subsequent expansion ('Leçons de Mécanique Céleste,' vol. 1, 1905, pp. 172, 198, 268). There is a further theorem of great importance which, like the proof of the divergence of Lindstedt's series, occurs in Poincaré's prize essay. The problem of three bodies has the classical integrals, which belong to any dynamical system, known as those of energy and momentum. It was proved by Bruns that, apart from and independent of these, the problem allows no other algebraic integral. To this Poincaré adds the theorem that the problem possesses no single-valued integral. The statement is for certain restricted values of the parameters; upon these restrictions we need not now enter.

This account leaves aside many matters dealing with the theory of orbits to which Poincaré devotes attention, and it does not represent his whole contribution to Astronomy. For very soon after the publication of the paper dealing with periodic orbits (Bull. Astr., vol. 1, 1884) Poincaré was publishing investigations issuing in 1885 in a great paper (Acta Math., vol. 7) dealing with the forms of rotating masses of fluid and their stability. As his investigations in regard to periodic orbits begin with acknowledgments to G. W. Hill, so this paper begins by quoting the results announced by Thomson and Tait in the 'Natural Philosophy,' Without entering into precise mathematics it would seem to be impossible to give here any competent account of Poincaré's work; the questions of stability involved are still matter of controversy. Poincaré considers a series of possible shapes of relative equilibrium, bestowing especial care upon the critical values of the parameters. We is thus led to consider the possibility of Jacobi's ellipsoid of

unequal axes changing gradually into a shape which may be likened to a pear spinning about a line at right angles to its long axis. The suggestion is that the thinner portion (the stalk end) may gradually become detached. reader will find it interesting to turn to the remarks made by Sir George Darwin in presenting to Poincaré the gold medal of the Royal Astronomical Society, in 1909. It was a subject upon which no one could speak with greater authority. Evidently Poincaré's investigation was to him a revelation of intellectual mastery for which he had the profoundest respect. Besides this work there remains, however, also Poincaré's work in regard to tides. It may be sufficient, perhaps, to refer to Sir George Darwin's brief indication of his concurrence, in this matter, with what is undoubtedly a very common feeling in regard to much of Poincaré's applied mathematics, namely, that the great generality of his methods is apt to militate against any quite immediate application. Undoubtedly he has no scruple in bringing the most advanced and the most modern theories of pure mathematics into service; and where such theory is not already in existence he invents it.

When we turn from Poincaré's astronomical work to his work in Physics, we enter upon ground which has already been much trodden. It may be sufficient to call attention to the large number of volumes of Sorbonne lectures, edited by his pupils, dealing freshly with the whole field of recent discovery and discussion in electricity, optics, thermodynamics, beside those dealing with matters already referred to.

But in addition to all this mathematical and physical work, Poincaré was also a prolific writer on general questions of philosophic interest. How far his contribution to these matters was new, and how far he stated in a brilliant way the critical conclusions which are common to many to-day, it must be for others to decide. At least, while taking up the humblest and simplest attitude in face of the immensity of the universe, he preached in no uncertain way the dignity of the pursuit of truth. "Thought is the lightning flash between two infinities of blackness. But it is the lightning which matters."

His writings on such matters are accessible to all and of general interest. It is unnecessary to expound them here.

H. F. B.

SIR ROBERT STAWELL BALL, 1840-1913.

ROBERT STAWELL BALL was born at Dublin on July 1, 1840. His father, Dr. Robert Ball, was born at Cove, co. Cork, in 1802, from whence he migrated to Dublin in 1827 upon his appointment to a post at the Castle. Dr. Ball took a keen interest in Natural History, and the Dublin Zoological Gardens are largely due to his persevering and unstinted labours. He died at a comparatively early age in 1857, leaving a widow and seven children, three sons and four daughters. Robert Stawell was the eldest of the sons, who all became distinguished citizens of Dublin, Dr. Valentine Ball becoming the Director of the Science and Art Museum, and Sir Charles Ball the well known surgeon.

After some years at a preparatory school in Dublin, Robert was sent in 1851 to Dr. Brindley's school at Tarvin, near Chester, where he received his early training in Mathematics from the Rev. Theophilus B. Rowe, afterwards headmaster of Tonbridge School. He remained at Tarvin till his father's death. In October, 1857, he was entered as a student at Trinity College, Dublin. He soon showed his aptitude for Mathematics and won numerous prizes. In 1860 he obtained a scholarship and the Lloyd Exhibition. In 1861 he was Gold Medallist in Mathematics, first Gold Medallist in Experimental and Natural Sciences, and University Student. He competed three times for a Fellowship at Trinity College, but was not successful, the successful candidates on two of the occasions being W. S. Burnside and H. S. Tarleton.

Ball's interest in Astronomy was awakened by Mitchell's 'Orbs of Heaven, a book he read at school at a time when he should have been asleep. At college he studied Brinkley's 'Astronomy,' the 'Principia,' and the 'Mécanique Celeste.' In 1865, at the instance of Dr. Johnstone Stoney, he was invited to become tutor to the sons of Lord Rosse at Parsonstown. He accepted the post on the condition that he should have access to the Observatory and the privilege of using the great telescope. He worked with the 6-foot reflector from January, 1866, to August, 1867, making micrometer observations of the positions of small nebulæ. It is pointed out by Dr. Dreyer that he was the first observer with the instrument to correct the observed position angles for the error due to the instrument not being equatorially mounted, but supported at its lower end by a universal joint, the fixed axis of which was horizontal, in the east and west direction. This procedure, which materially improved the observations, was a natural outcome of Ball's geometrical instincts. About this time the application of the spectroscope to the problems of Astronomy was making great headway. Although Sir Robert Hall took no active part in this, he was keenly interested in it, an interest quickened by a visit to Sir William Huggins' Observatory at Dulwich.

In 1867 the Royal College of Science was founded in Dublin, and Ball left Birr Castle to become the first Professor of Applied Mathematics and Mechanism. He was well fitted for this post by his mathematical knowledge and ability and his experimental skill, but especially by his gift for lucid exposition. He was one of the first in Great Britain to introduce the system of C.G.S. units in his class teaching. In addition to his class lectures he gave some evening lectures of a more elementary character, and here showed and developed his genius as a popular lecturer. In 1871 he published a work on 'Experimental Mechanics,' the outcome of his evening lectures. This was the first of the many popular books he wrote.

In 1870 Ball read a paper before the Royal Irish Academy on "The Small Oscillations of a Rigid Body moving about a Fixed Point under no Forces." This was the first of his many memoirs on the theory of screws. The whole series was published in a single volume by the Cambridge University Press in 1900. A critical account of this important contribution to Mathematics is given at the end of this notice.

In 1874 Ball was appointed successor to Brünnow as Royal Astronomer of Ireland and Andrews Professor of Astronomy in the University of Dublin. The Observatory, situated at Dunsink, a few miles from Dublin, possessed an excellent 12-inch telescope, the gift of Sir James South. This had been employed by Brünnow in the investigation of stellar parallax, a branch of astronomy which his predecessor Brinckley had attempted half a century previously. Dr. Ball decided to pursue this important but difficult research, and commenced with the star 61 Cygni, for which he obtained a result in good agreement with the classical determination by Bessel. From 1876 to 1881 he prosecuted an active search for stars of large parallax. In all, 368 stars were examined and the results published in the Dunsink Observations. In the preface to this memoir he states: "It is, of course, well known that up to the present no parallax of a star has been detected which exceeds one second of arc. In the majority of cases the parallax is much less, even if it is appreciable. But when we reflect that not one star out of every 10,000 has yet been regularly examined for parallax, it is obvious that it would be rash to conclude that there are no stars nearer to us than any of those of which we already know the distance." The results he obtained were negative, but it was nevertheless of interest to demonstrate that none of the stars presumably near the solar system were so close as to have a parallax as great as one second. The more refined observations of the heliometer and the photographic refractor were shown to be necessary for the measurement of the small displacements of even the nearest stars.

In February, 1892, Sir Robert Ball succeeded Prof. Adams in the Lowndean Chair of Astronomy and Geometry and the Directorship of the University Observatory at Cambridge. During his directorate the valuable catalogue of stars, commenced in Adams' time, was completed and published by Mr. Graham. A photographic telescope, mounted on a novel plan according to a design by Dr. Common, was erected for the purpose of carrying on researches in stellar

parallax. This instrument was put to very efficient use by Mr. Hinks in observations of the planet Eros in 1900 and 1901 for the determination of the solar parallax, and by Mr. Hinks and Prof. H. N. Russell (then an advanced student of the University) for observations of stellar parallax. Sir Robert Ball maintained an interest in these parallax researches, but left their active prosecution to Mr. Hinks and Mr. Russell.

As a lecturer on Mathematical Astronomy, Sir Robert Ball gave his pupils a lucid exposition of the classical writers on celestial mechanics. He wrote a text-book on 'Spherical Astronomy,' intended for the use of University students. This book contains a chapter on the theory of astronomical instruments, which is of special interest, as showing the geometrical bent of hisjmathematical interests.

Sir Robert Ball rendered great service by his popular books and lectures. These awakened an interest in astronomy among a very wide circle of readers and hearers. A lecture which he delivered at the Midland Institute at Birmingham in 1881 attracted particular attention and established his fame as a popular expositor of science. This lecture, entitled, "A Glimpse through the Corridors of Time," gave in popular language an outline of Sir George Darwin's theory of the tidal evolution of the Moon. As a lecturer he possessed great lucidity and brought abstruse subjects within the comprehension of his audiences. His delightful gift of humour was always at hand to enliven any dull parts of a lecture and retain the attention of his hearers. He lectured in most of the large towns in Great Britain and in many cities of the United States and in Canada. Probably more than a million people have heard him lecture.

Among his many popular books, 'The Story of the Heavens,' published in 1886; 'The Story of the Sun,' published in 1893; and 'Great Astronomers,' published in 1896, may be specially mentioned. They are written in a very pleasant style, and the lives of Astronomers, including those of Hamilton and Adams, his predecessors at Dunsink and Cambridge, are told in a delightful manner.

In 1884, Ball became Scientific Adviser to the Commission of Irish Lights, in succession to Tyndall, and always took the greatest delight in the annual cruise of the Commissioners round Ireland to inspect the lighthouses. In 1886 the honour of knighthood was conferred upon him. He was elected a Fellow of the Royal Society in 1873 and served on the Council in 1897–8. He was President of the Royal Astronomical Society, 1897–9.

In 1868 he married Frances Elizabeth, daughter of the late Dr. W. E. Steele, Director of the Science and Art Museum, Dublin. He leaves four sons and two daughters.

Sir Robert Ball died at Cambridge on November 25, 1913, after an illness which lingered for over two years. He was a most warm-hearted and kindly man and had a large circle of friends attracted by his genial manner, ready sympathy, and delightful humour.

Ball's 'Theory of Screws' gives a very complete geometrical treatment of the problems of small movements in rigid dynamics, and in that respect is unique among English books. The small first edition appeared in 1876. Ten years later was published the German 'Theoretische Mechanik Starrer Systeme' of Gravelius, founded mainly upon Ball's memoirs. The "twelfth and concluding" memoir in the Proceedings of the Royal Irish Academy was dated 1898, and the large and comprehensive work on the 'Theory of Screws' was published in 1900.

The keynote to the whole method consists in the use of the "screw," consisting of a line in space together with an associated length. geometric entity has a double use. It gives the axis and the pitch of either a "wrench," representing any system of forces, or of a "twist," representing the most general small displacement of a rigid body. The derivative relationships of which the method is built may be briefly described. screws are defined as "reciprocal" when a wrench on one screw does no work for a twist on the other, and so also conversely. A "principal screw of inertia" is such that an impulsive wrench on it produces instantaneous twist on the same screw. "Conjugate screws of inertia" are such that a twist on either is produced by an impulsive wrench on a screw reciprocal to the other. Similarly for the forces of restitution: a "principal serew of potential" is such that a twist on it evokes a wrench on the same screw. and "conjugate screws of potential" are such that a twist on either evokes a wrench on a screw reciprocal to the other. A "harmonic screw" is such that a twist on it evokes a wrench which produces a twist on the screw itself. A harmonic twist on such a screw is thus one of the normal modes of oscillation of the body about its position of equilibrium. These relationships are intimately connected with the "kinetic screw complex," consisting of the screws for twists on which the kinetic energy is zero, and the "potential screw complex" for which the potential energy is constant.

With this apparatus a thorough investigation is made of the behaviour of a rigid body with any number of degrees of freedom from one to six. In the case of two degrees of freedom the notable "cylindroid" presents itself, as the cubic surface locus of the screw-axes of all possible twists. But the cylindroid is used fundamentally through the whole work, and a perspective view of the surface figures naturally as a frontispiece to the volume. Though not the actual discoverer of the surface (Hamilton and Plücker had found its chief property earlier), Ball certainly counts as its chief patron. He took always a lively interest in any development of its properties, and a beautifully made model placed in the collection of Cambridge University serves as a memento of its former owner.

If the geometry of the linear complex had developed earlier, its immediate application to infinitesimal rigid dynamics should have followed as a logical consequence; but the subject was in its infancy, and Ball had to investigate much of the geometry for himself as he progressed. This he was well able to do, and he seems to have made independent discovery of some of

the theorems of line-geometry. The conciseness and elegance, in particular, of the treatment of the case of two degrees of freedom by a circular diagram represents evidently his native geometric faculty. Perhaps some of the later developments seem less natural. Any general system of bodies is dealt with under the description of a "screw-chain"; but the arbitrary assignment of a definite sequence to the bodies forming the chain seems artificial as a mode of treatment. In the case of the so-called "permanent screws" the terminology at least seems inapt, for the "permanence" is only transient.

For a most admirable and appreciative survey of the scope of Ball's work on screws, reference may be made to a review by Henrici ('Nature,' June 5, 1890, pp. 127-132) of the German treatise above mentioned. An excellent account was given by Ball himself in his presidential address to the Mathematical Section of the British Association in 1887. He there uses some geometrical abstractions, quaintly personified, as speakers in a discussion; and, under this whimsical garb, reveals the essence of his methods very pertinently and clearly. Through all Ball's work there shows a fine enthusiasm for his subject and a most generous appreciation of the discoveries of others. In the year 1879 the Royal Irish Academy awarded him the Cunningham Gold Medal, and his name thus occurs in a list which includes also those of Casey, MacCullagh, Hamilton, Jellett, and Salmon. By his many and excellent contributions to the geometry of kinematics and dynamics, Robert Stawell Ball assuredly takes an honourable place on the roll of Irish mathematicians.

F. W. D. and G. T. B.

LORD STRATHCONA AND MOUNT ROYAL, 1820-1914.

SIR DONALD ALEXANDER SMITH, Baron Stratheona and Mount Royal, died on January 21 last in the 94th year of his age.

He was a man of very strong personality, who wrought out for himself a striking and remarkable career, achieving success in many different paths, but having ever in view the welfare and progress of the Empire as a whole.

He was born at Forres, in the Scotch Highlands, on August 6, 1820, and was the second son of Alexander Smith, a merchant of Archiestown, and Barbara Stewart, whose brother, John Stewart, was a well known fur trader in the North-West Company, having its headquarters in Montreal.

After receiving a good elementary education at the school at Forres, it happened that on one occasion he visited Manchester in company with a friend of the rising young London novelist, Charles Dickens, and made the acquaintance of a wealthy and highly esteemed family of merchants named Grant, who were cousins of the Smith family.

These two warm-hearted men have been introduced to the world under the name of the Cheeryble Brothers by Dickens. He was about to enter the office of this firm when his uncle, John Stewart, returned to Scotland, and through his influence Donald Smith was appointed to a junior clerkship in the renowned Hudson's Bay Company, which at that time controlled the greater part of what has since become the Dominion of Canada. He was 18 years of age at this time. The passage out to Canada occupied rather more than six weeks, while his return passage to England on the "Mauretania" shortly before his death occupied approximately six days.

Upon his arrival he was sent to Labrador, one of the most remote and inaccessible districts occupied by the Company, where he remained for 13 years at one or other of the Company's posts, engaged in trading with the Montagnais Indians and such Eskimos as inhabited or visited that most inhospitable coast.

He was then promoted to the position of Chief Trader in the Company's service, and after 10 years more spent on the shores of Hudson Bay he became a Chief Factor of the Company, and in 1868 became Chief Executive Officer of the Company, with his headquarters in Montreal, where he took up his residence, being now 48 years of age.

The fact that the great prairies of Central and Western Canada were suitable for settlement was becoming generally recognised by the people of Canada at this time, and negotiations were opened up in this year for the surrender of the lands of the Hudson Bay Company to the Government of the Dominion of Canada. When, however, the Deed of Surrender was signed and the agents of the Government proceeded to Fort Garry (now Winnipeg),

the ignorant half-breeds, who with the Indians were the only residents of the eastern prairies at that time, thinking that the Government intended to deprive them of their lands, rose in revolt under a half-breed named Louis Riel, purposing either to establish an independent government or to take steps to have the country annexed to the United States. Donald Smith was sent to the scene of trouble with a view to explain the situation to the half-breeds and allay their fears. Upon his arrival at Fort Garry, he was seized by Riel and held as a prisoner for about two months. He was, however, so far successful in carrying out his commission that, while the Government found it advisable to send a small expedition under Colonel (afterwards Viscount Sir Garnet) Wolseley to the scene of the disturbance, upon the arrival of the troops Riel fled to the United States and the revolt came to an end without a blow having been struck.

Upon the collapse of the Riel rebellion, Donald Smith was elected to represent the constituency of Selkirk, one of the electoral divisions of this new territory, in the Dominion House of Parliament.

About this time, in the early seventies, the necessity of building a transcontinental railway to open up this great western prairie country and especially to open up communication between British Columbia and the rest of the Dominion became evident. In fact, one of the conditions under which this colony came into the Canadian Confederation was that such a railway should be built within a period of 10 years after the agreement had been At the inception of this great enterprise Mr. Smith strongly advocated the policy that the road should be built by the Government of Canada and not by a private company. But when both parties who came successively into power failed to make any substantial progress with the work, he recognised that unless some company with the requisite initiative and capital took the work in hand, the project would certainly not be realised within any reasonable time. In fact, the failure of the Government to carry through this great undertaking which they had commenced left Manitoba and the other prairie provinces without any means of communication by railway with the outside world, and in order to immediately supply this pressing need Donald Smith associated with himself a few other far-seeing men and secured the control of the bankrupt and abandoned St. Paul and Pacific Railway which had been built from St. Paul in the State of Minnesota to a point not far from the Canadian boundary. This having been done, the road, under the name of the St. Paul, Minneapolis and Manitoba Railway, was completed to Winnipeg, thus giving the needed outlet. The great development of this road subsequently brought very large financial returns to the gentlemen who had possessed the foresight to construct it.

In 1880 a syndicate was formed to take over the Canadian Pacific Railway from the Government, who had barely commenced the road, and to complete it. Although Mr. Smith's name did not appear as one of the contracting parties, it was largely his energy, determination, and financial assistance in times of great difficulty that carried the enterprise to a successful conclusion.

"We had," he writes, "of course, a good deal of anxiety while the work was going on, but we were sustained by the knowledge that it was approved of and supported by Canada as a whole, and that an important step was being taken not only in developing the resources of the country, but also in bringing Canada closer and yet more close to England and our sister colonies, thus forming a means of cementing together the various parts of the Empire." He formally completed the building of the railway by driving the last spike on November 7, 1885.

The year following Her Majesty bestowed upon him a knighthood of the Order of St. Michael and St. George; in 1896 he was created a Knight of the Grand Cross of the same Order, and the following year he was raised to the peerage as Baron Stratheona and Mount Royal.

Upon the outbreak of the Boer War Lord Strathcona raised in Canada a regiment of mounted infantry, numbering about 600 and recruited largely from the North-West Mounted Police, known as the Strathcona Horse, which was equipped and transported to Africa at his own expense. They were attached to Lord Dundonald's brigade.

Lord Strathcona's generosity knew no bounds. His benefactions were widespread not only in Canada but also in Great Britain. Montreal, which was Lord Strathcona's place of residence during most of his later years in Canada and one constituency of which (Montreal West) he represented during two Parliaments in the Dominion House, was the especial object of his munificence. In conjunction with Lord Mount Stephen he erected and endowed the Royal Victoria Hospital in that city in commemoration of Queen Victoria's Jubilee, which institution has by his will received a very large additional endowment. His benefactions to McGill University, of which he was Chancellor, were numerous. Among these may be mentioned the Royal Victoria College for Women, the new building which has just been erected for the Faculty of Medicine, and the endowment of the Strathcona Professorship of Zoology.

Lord Strathcona received the degree of LL.D. from the University of Cambridge in 1887, from Yale University in 1892, from the University of Toronto in 1903, from the University of Durham in 1910, and from St. Andrew's in 1911. In the year 1900 he was appointed Lord Rector of the University of Aberdeen.

He was elected a Fellow of the Royal Society in 1904, and was Honorary Vice-President of the Royal Society of Canada.

He was also well known as a lover of the Arts, his picture galleries containing well known works by many of the great masters. Together with Lord Mount Stephen he endowed a Canadian Scholarship in the Royal College of Music, London, and he subsequently endowed a second Scholarship on his own account.

From the year 1896 until his decease, Lord Strathcona, as High Commissioner for Canada, represented the Dominion in London, a position which he filled with dignity and honour. His age, his talents, his princely

benefactions, his wide sympathies, his wise and kindly philanthropies, his charming personality, and the admirable manner in which he represented Canada in Great Britain, endeared Lord Strathcona to the Canadian people in a very especial manner, and no one in the Dominion was ever so beloved by all. He gave a long life to the enlargement of the Empire and the knitting together of its strength.

F. D. A.

EARL OF CRAWFORD, K.T., 1847-1913.

James Ludovic Lindsay, 26th Earl of Crawford, was born in 1847. Among his many scientific and bibliographical interests, Astronomy took the foremost place during his most active years. He established and maintained at Dunecht, near Aberdeen, an observatory and an astronomical library that can have had few parallels for completeness. In this work, which began in 1872, Lord Lindsay, as he then was, worked in fortunate association and rival enthusiasm with David Gill, the son of an Aberdeen merchant, who had then already made his mark upon the science. The chief instruments were an 8½-inch transit circle, by Simms, a 15-inch equatorial, by Grubb (at that date a large aperture), many spectroscopes, and other physical apparatus. The library contained many treasures, and bibliographical notes in many of the books testify to Lord Lindsay's intimacy with them. One feature of the Dunecht observatory was the issue of circulars in which early information of astronomical events, the places of comets, and so forth, was conveyed to a number of other observers.

In 1874 Lord Lindsay, with Gill, organised an expedition to Mauritius to observe the transit of Venus. The results of the transit were disappointing, but incidentally a large amount of valuable longitude work was performed. In 1876, Gill was succeeded in the charge of the observatory by Dr. Ralph Copeland.

In 1880, Lord Lindsay succeeded to the earldom, and shortly after decided to part with his estate at Dunecht and remove his observatory to Balcarres in Fife. Circumstances arose which diverted his intention. On the resignation of C. Piazzi Smyth, the Royal Observatory at Edinburgh, then miserably housed on the Calton Hill, was in danger of extinction. Lord Crawford saved the situation by offering the whole of his magnificent collection, instruments, printed books, and manuscripts, to the nation, provided that a proper establishment was maintained. The gift was accepted, and the new observatory on the Blackford Hill was opened in 1896.

This terminated Lord Crawford's connection with Astronomy, but he was always a lover of books, and continued to make other bibliographical collections until his death. He was also well known as a yachtsman, and, in 1906, made an extended voyage in the South Atlantic and Indian Oceans collecting specimens of natural history.

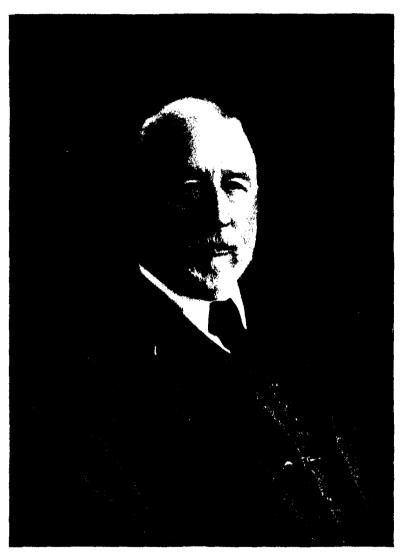
Lord Crawford was president of the Royal Astronomical Society in 1878 and 1879. In the former year he was elected a Fellow of our Society. As Baron Wigan he took an active part in the management of the Public Library at Wigan and enriched it by many valuable gifts. He died on January 31, 1913, and is succeeded by his son.

R. A. S.

SIR DAVID GILL, K.C.B., 1843-1914.

DAVID GILL, son of David Gill, J.P., of Blairythan, Aberdeenshire, was born at Aberdeen on June 12, 1843. He attended the Bellevue Academy in that city till he reached the age of 14, when he was sent to the Dollar Academy, where the teaching of Dr. Lindsay imparted to him a love of Mathematics, Physics, and Chemistry. He proceeded to Marischal College and University, Aberdeen, where his love of science was developed under the inspiring influence of Clerk Maxwell. In the 'History of the Cape Observatory,' published only a few months before his death, Gill tells of the pleasure he derived from Maxwell's teaching. After lectures, only perhaps partially understood, Maxwell would stay for hours in his lecture room with a few of the best students and discuss points which occurred to him or to them, or show them experiments he was making at the time. These conversations with Maxwell profoundly influenced Gill, and implanted in him a deep desire for a life of scientific investigation. This was not, however, realised at first. Gill's father, who had a prosperous old-established business in clocks, was anxious that his son should succeed him. Gill reluctantly consented and entered his father's business, of which after a few years he took complete charge. He consoled himself by devoting all his spare time to Physics and Chemistry in a small laboratory he had established in his father's house. With characteristic thoroughness, however, he mastered all the details of his business, and to the end of his life kept on his study mantelpiece a beautiful clock made with his own hands.

His special interest in Astronomy began in 1863. It occurred to him that a time service in Aberdeen such as Piazzi Smyth had established in Edinburgh would be of great value to the city. He discussed the matter with David



MOFFAT, PHOTO, EDINBURGH

David Gile.

Thomson, Professor of Natural Philosophy in King's College, Aberdeen. Thomson gave him an introduction to Piazzi Smyth, whom he visited at Edinburgh. Here he was shown not only the arrangements for the timegun and ball, but all the instruments of the Observatory on the Calton Hill. From that day he took a new interest in Astronomy, and, on his return to Aberdeen, proceeded with Prof. Thomson to re-establish the disused "Observatory" of King's College. A small portable transit-instrument was unearthed, mounted on its piers and adjusted. The Observatory possessed a good sidereal clock. A mean solar clock was added, with arrangements for altering its rate, so that it could be kept within a fraction of a second of Greenwich time. Contact springs were fitted to it so that electric currents were sent each second, and in this way the turret clock of the college and other clocks in the town were controlled.

When the time service had been got into working order, a Dallmeyer telescope of 34 inches aperture and 4 feet focus was obtained for the College, and Gill made some micrometric observations of double stars. Although the object glass was good, the mounting was too weak for the observations to be quite satisfactory. Gill therefore purchased for himself, from the Rev. Henry Cooper-Key, a speculum of 12 inches aperture and 10 feet focus. He designed an equatorial mounting himself, and had the heavy parts of the instruments made to his own working drawings by a firm of shipbuilders in Aberdeen. The driving circle, its tangent screw, and slow motion, as well as the declination circle, were made by Messrs. Cooke, of York. The driving clock, which he made with his own hands, was on the same general plan as Airy's chronograph at Greenwich. This was his first experiment in the design and construction of astronomical instruments, and it is interesting to note that in the course of his life he never came across a driving clock which worked more satisfactorily. The instrument was employed in the observations of double stars and nebulæ, and in photographs of the Moon. One of the latter, which he presented to Sir W. Huggins, has recently come into the possession of the Royal Astronomical Society and is of great excellence.

In 1870 he married Isobel, second daughter of Mr. John Black, Linhead, Aberdeenshire. They settled in the town of Aberdeen, near the Observatory. Shortly after their marriage Gill was faced with the alternative of continuing in a prosperous business and working at Astronomy as an amateur after business hours, or of following his own inclinations, and giving this up for a much smaller income and the opportunity of devoting his time exclusively to science. The decision he took with Mrs. Gill's full approval and support, and which they never regretted, was to make the pecuniary sacrifice so that Gill's deep interest in Astronomy might be fully gratified.

The occasion of this change in Gill's position arose through a friendship which had grown up between him and Lord Lindsay, who was interested in Gill's photographs of the Moon and afterwards attracted by his scientific enthusiasm. Lord Lindsay was an enthusiastic amateur astronomer and

proposed to erect a private observatory at Dunecht. In 1872, his father, the Earl of Crawford and Balcarres, wrote to Gill offering him the charge of this observatory. Gill gratefully accepted the offer, and, when his business affairs were wound up, moved to Dunecht. Here he was soon engaged on the congenial task of the design and erection of the fine private observatory which Lord Lindsay projected.

The years 1872-74 were busily employed in the equipment of the observatory. This comprised a 15-inch refractor by Grubb, an 8-inch reversible transit circle by Troughton and Simms, a 12-inch mirror which Gill had at Aberdeen, a 4-inch heliometer by Repsold, and a number of smaller instruments. Preparations were also made for an expedition to Mauritius to observe the transit of Venus in 1874. In connection with this expedition and the building of the observatory at Dunecht, Gill paid visits to most of the European Observatories. Thus acquaintanceships were made which ripened in several cases to a lifelong friendship.

In view of the possibility of the British station at Mauritius becoming a central one to which the longitudes of surrounding stations would be referred. Lord Lindsay decided that the longitude of Mauritius should be determined with as much accuracy as possible. He and Gill proposed to determine the longitude Greenwich-Aden telegraphically, and Aden-Mauritius by the transportation of chronometers. The section Greenwich-Aden was completed by the chain Greenwich-Berlin-Malta-Alexandria-Suez-Aden. The time determinations at the intermediate stations had to be made between the arrival and departure of steamers. A theodolite mounted on a tripod was employed by Gill, and subsequent determinations have shown the great accuracy of the results he obtained with this small instrument. The carriage of the chronometers was a matter of some difficulty, especially their embarkation and landing at ports where only coloured labour was available. No less than fifty were hired from the leading makers, very carefully packed and mounted, compared before starting, and then carried with incessant watchfulness from Greenwich-Aden, Aden-Mauritius, and back again.

The main interest of the expedition to Mauritius centres in the heliometer observations of the minor planet Juno, which were made for the determination of the solar parallax. As Lord Lindsay's arrival with the heliometer was delayed by unfavourable winds, the observations could not be begun till a week after opposition. 'Nevertheless, after a series of observations extending over 12 evenings and 11 mornings, the value 8.77 seconds was obtained for the solar parallax with a probable error ±0.041 sec. The discussion of these observations gave Gill a profound conviction of the possibilities of the heliometer for measurements of great refinement, and influenced his future work very materially. Thus, although the observations of the transit of Venus failed in their direct object, this expedition became the starting point of a method by which the Sun's distance has since been determined with the highest accuracy.

On the return journey from this expedition Gill obtained his first experi-

ence in geodetic work. While he was at Mauritius, he was invited by General Stone, Chief of the Military Staff of the Khedive, to return through Egypt and measure the base line for the survey which was projected. With Lord Lindsay's ready assent, Gill undertook this task, and, with the assistance of the American astronomer, Prof. Watson, who happened to be at Cairo, laid down a base line near the Sphinx, using a base-measuring apparatus belonging to the Egyptian Government constructed by Brunner, of Paris.

The next great piece of work which engaged Gill's attention was the determination of the solar parallax from the exceptionally favourable opposition of Mars in 1877. He was aware of the advantage which a minor planet possessed for this purpose, owing to its having no perceptible disc, but the geometrical conditions of the opposition of 1877 were so favourable that he considered that the opportunity of utilising it was not to be missed. Although Gill had left Dunecht in 1876, he had obtained from Lord Lindsay the loan of his heliometer, conditionally upon his obtaining the means to undertake this expedition.

The sum of £500 was provided, half by the Royal Astronomical Society and half by the Government Grant Fund of the Royal Society. The Island of Ascension was chosen as the station for observation, as its latitude (8° south of the equator) made the base line obtained from evening and morning observations of Mars a large one, and on account of the south declination of Mars. Lady Gill accompanied her husband and wrote a delightful account of the expedition,* which gives a picture of its incidents and anxieties. They were on the island for seven months. At first the Observatory was set up at Garrison. Lady Gill writes:—

Fearful of losing one hour of starlight we watched alternately for moments of break in the cloud, somotimes with partial success, but more frequently with no result but utter disappointment, and the mental and physical strain, increasing every night, grew almost beyond our strength when one day David spoke and took away my breath. He said, "Let us prove how far this cloud extends and find out whether there is any accessible part of the island not covered by it."

The clouds only came up at night, and Gill could not leave the Observatory at a time so near opposition. He yielded to his wife's wish that she should make the necessary exploration. Lady Gill found a spot in the south-west corner of the island much freer from cloud. But this was difficult of access. The surf made landing from the sea only possible now and then, and the transport of instruments which could not be repaired, if injured, over rocky country without roads was not to be lightly undertaken.

On the one hand my husband felt, If I stay here and fail, I shall have failed also in my duty, not having done my utmost. On the other hand, every night is now of importance, and a week is lost certainly, if I pull down the Observatory, while the slightest accident to an instrument here, with no one to repair it, will be fatal to the

^{* &#}x27;Six Months in Ascension: An Unscientific Account of a Scientific Expedition, by Mrs. Gill. John Murray, London, 1878.

expedition. Yes! both "ifs" were unpleasant, but the first was intolerable, and after a day of anxious thought David made up his mind that an attempt to reach South Point must be made.

The Observatory was moved without accident to the new site, which they called Mars Bay, and only five days elapsed before successful morning and evening observations were made.

This laborious and difficult enterprise was crowned with success. The solar parallax was determined as 8.78 seconds, with a probable error of + 0.012 second, a considerable advance on previous determinations; but Gill's experience convinced him that for a definitive determination a minor planet must be used, as it was impossible to set a star on the limb of the planet without danger of systematic personal error. A second important result of the investigation was the clear evidence afforded by comparison of the positions of the reference stars obtained by transit circle observations with their relative positions given by the heliometric measurements that there was among meridian observers a personal equation depending on the magnitude of the star, whose general tendency was to make faint stars late relatively to bright ones. This "magnitude equation," suspected by Bessel and investigated to a certain extent by Argelander, is of special importance wherever meridian observations are used in conjunction with others, whether heliometric or photographic. Its serious consideration dates from this time. and modifications have since been introduced into methods of observing for the purpose of its elimination.

In 1879 Gill was appointed H.M. Astronomer at the Cape. He possessed unrivalled skill as an observer, was never satisfied with anything less than the most accurate work, and spared no pains to avoid all errors of systematic character. His engineering and mechanical skill added greatly to his qualifications for the directorship of an observatory which needed to be re-equipped. But the qualities which marked him out for success in this new post were his abounding energy and enthusiasm and his resolute perseverance. Immediately after his appointment he visited the observatories at Paris, Leiden, Groningen, Hamburg, Copenhagen, Helsingfors, Poulkova, and Strassburg, learning the aims and methods of different astronomers and coming into touch with them. He was particularly impressed by Winnecke at Strassburg, whom he regarded as the greatest astronomical teacher of the day, and by the earnest band of students whom he had gathered around him.

The Cape Observatory had been founded in 1820 by the Lords Commissioners of the Admiralty on the recommendation of the Board of Longitude. Fallows, the first of His Majesty's Astronomers, established the Observatory on a bare, rocky hill, within sight of Table Bay, and commenced meridian observations of the positions of stars and planets. He died in 1831, and was succeeded by Henderson, who in one year made a large number of valuable observations of stars, and whose name is associated with his discovery of the distance of a Centauri. Henderson was succeeded

by Maclear, whose directorate lasted from 1833 to 1870; Maclear added magnetic, meteorological, and tidal observations to the work of the Observatory and commenced the geodetic survey of South Africa. Stone devoted his attention (1870–1879) mainly to a great catalogue of 12,441 stars, in which he re-observed all the stars observed by Lacaille in 1763.

The national character of the Observatory made the continuance and improvement of meridian observations an essential part of the work of the Cape Observatory. The traditions left by Maclear and Henderson suggested that geodetic investigations and determinations of stellar parallax ought to be carried out. Researches in both of these directions were in harmony with Gill's tastes and previous experience. During his stay at the Cape the whole of this programme was carried out. Old meridian observations were reduced and published, a new instrument embodying new and most useful features was installed; the geodetic survey of South Africa was co-ordinated, and a work of fundamental importance towards the determination of the size and shape of the Earth initiated; the distances of the Sun and a number of stars were determined with unexampled precision. In addition, at least three very valuable projects were executed, which were not foreseen in 1879, the 'Cape Photographic Durchmusterung,' the 'International Photographic Chart of the Heavens,' and the establishment of a large telescope for spectroscopic and other work. To these projects Gill gave both guidance and driving force.

Soon after his appointment to the Cape, Gill bought from Lord Crawford the 4-inch heliometer with a view of commencing forthwith researches on stellar parallax. In this work he secured the assistance of a young American astronomer, Mr. W. L. Elkin, a pupil of Winnecke's, who had selected 'The Parallax of a Centauri' as the subject of his dissertation for his Doctor's degree. Elkin went to the Cape in January, 1881, and stayed there 18 months as a guest of Dr. and Mrs. Gill. Nine stars were chosen as suitable for parallax determinations on account of their brightness or large proper motion. Gill and Elkin decided that three of these stars, a Centauri, Sirius, and a Indi, should be observed by both of them, but using different comparison stars, in order to furnish a check on possible systematic errors. The results obtained from this arduous and very skilful observing were very valuable. The distances of a Centauri and Sirius were determined to within a small percentage of the total amount, and Canopus, the brightest star in the sky except Sirius, was found to be at a great distance, not less than a hundred times that of Sirius. The high accuracy obtained with this small telescope is very remarkable, but its use was found by experience to be hampered by the small field, which limited the choice of comparison stars. Gill therefore urged upon the Admiralty the desirability of obtaining a larger instrument, and the purchase of a 7-inch heliometer was sanctioned. This was constructed by Messrs. Repsold, of Hamburg, who embedded in their design a number of improvements and refinements suggested by Gill's experience. The instrument was completed in 1887 and housed in an observatory specially built for it. The programme which Gill set before himself was not so much to determine the parallax of individual stars as to find out what general relationships existed between the parallaxes of stars and their magnitudes and the amount of their proper Work was therefore first directed on the brightest stars of the Southern Hemisphere. The actual observations, involving much painstaking and trying work for some hours after sunset and before sunrise, were carried out largely by Gill himself. One star was wholly observed by Mr. Finlay, Chief Assistant at the Observatory, and two stars were observed by both Gill and Finlay. In 1897, Mr. W. de Sitter, a pupil of Prof. Kapteyn's, joined the staff of the Cape Observatory for a short time, and, among other observations with the heliometer, determined the parallaxes of four stars of large proper motion. The results of the researches on stellar parallax were published in a volume of the 'Cape Annals' in 1900. This contains all the determinations of parallax of stars in the Southern Hemisphere, and comprises the 12 stars brighter than the second magnitude, and 10 stars selected on account of their large proper motions. The 10 quick-moving stars all proved to be comparatively near, but the brightest stars were found to be at very great distances, except a Centauri, Sirius, and a Piscis Australis, all of which have considerable proper motions. The accuracy of the work may be said to mark an era in the determination of stellar parallax. It is exceeded, but not greatly, by the best photographic determinations, but these are made with very much larger telescopes, and, of course, with much less trouble. This precision is, in part, due to Gill's great personal skill as an observer, and, in part, to the admirable design of the instrument. He was not content to make many observations with small apparent error, but investigated, or eliminated, all causes introducing error of systematic character.

The success which had attended the observations of Juno in Mauritius and Mars in Ascension made Gill desirous of using the 7-inch heliometer at the first available opportunity to determine the solar parallax by observations of a minor planet when in opposition. The solar parallax enters as a coefficient into various terms in the theories of Sun, Moon and planets, and may therefore be deduced from the observed values of these terms. It is also derivable from the value of the constant of aberration, the velocity of light being obtained from laboratory measurements. But it was of great importance to determine this fundamental constant by direct geometrical methods, and to show that the value agreed with, or wherein and why it differed from, the value found in less direct ways. The transit of Venus of 1874, on which great hopes had been placed and on which very large sums of money had been spent in equipping expeditions to all parts of the world, had proved very disappointing. The various phases of the transit did not admit of sufficiently precise observation, a fact forcibly illustrated by the different results, 8.76 seconds and 8.90 seconds, derived by Airy and Stone respectively from the same observations. Looking forward to the available opportunities, Gill found that a favourable opposition of Iris would occur in 1888 and of Victoria

and Sappho in 1889. The co-operation of the Yale Observatory was secured for observations of Iris, and suitable comparison stars were chosen so that simultaneous observations should be made in the evening at Yale and in the morning at the Cape. This plan was slightly modified by the addition of the Radcliffe Observatory, Oxford, and the Leipzig Observatory to the schemes, and a number of evening observations were made at Yale for comparison with these. Between October 10 and December 13, 1888, over 1000 measures were made of the distance of the planet from various comparison stars at the four observatories, and were utilised for the determination of the solar parallax. The resulting value from a discussion by Dr. Elkin was 8.812 seconds, with a probable error of ±0.009 second.

For the observations of Victoria a very complete programme was devised, involving the co-operation of many observatories. It was desired to obtain the relative positions of the comparison stars with such accuracy that the error in the resulting parallax arising from the uncertainties in the framework of reference points should be negligible. Thus the errors would be confined to those of the heliometer measures of the distance of the planet from the stars and to errors in the ephemeris. Meridian observations of the stars were secured at no less than 20 observatories. These were combined by Dr. Auwers so as to give the best positions of the stars. The declinations were sufficiently good, but the right ascensions showed somewhat large discrepancies. Accordingly a heliometric triangulation of the stars was made by Gill, Elkin and Schur in 1890. By this means the weight of the position of the reference stars was largely increased, and the probable error of the final results reduced to ±0.03 second. The actual observations of Victoria were made at the Cape by Gill and Auwers, at Yale by Elkin and Hall, at Leipzig by Peter, at Göttingen by Schur, and at Bamberg by Hartwig.

A preliminary discussion of the observations showed that the errors of the ephemeris computed by the aid of 7-figure logarithms from Leverrier's tables of the Sun were greater than those of the observations. A new ephemeris was constructed at the office of the 'Berliner Jahrbuch,' using 8-figure logarithms, and paying special attention to the accuracy of the terms depending on the position of the Moon. The value of the solar parallax derived from the observations of Victoria was 8.8013 seconds ± 0.0061 second, and it is of interest to note that the Cape observations alone gave an identical result, 8.8014 seconds, with the larger but still very small probable error of ± 0.0108 seconds.

The observations of Sappho did not form so complete a series as those of Victoria, nor was the ephemeris constructed with the same care. Nevertheless a very accordant series of observations at the Cape and the four Northern observatories gave the result 8.7981 seconds, in satisfactory agreement with those obtained from Victoria and Iris, and with a probable error of \pm 0.0114 second. The final result for the solar parallax found from the three planets was 8.804 seconds, with a probable error slightly less than \pm 0.005 second.

Only one criticism has been urged against the acceptance of this probable error as a measure of the real accuracy of this result. It was urged by Prof. Newcomb that if the mean wave-length of the light of a minor planet were somewhat different from that of the comparison stars, then atmospheric dispersion would introduce a systematic error into the result. this by the assertion that an observer with the heliometer unconsciously matched the different colours of the very small spectra into which the images were dispersed, when he superposed one image over the other. In support of this contention he chose the very red star, & Sagittarii, and had its distance measured from comparison stars when it was at different altitudes by Mr. de Sitter and Mr. Lowinger. No perceptible effect arising from atmospheric dispersion was detected, and he therefore concluded that the effect must be negligible in the case of Victoria and Iris, which were to the eyes indistinguishable in colour from their comparison stars. value of the solar parallax has been confirmed by the observations of Eros and by a determination made at the Cape from spectroscopic observations of the velocity of the Earth in its orbit.

When the observations of Iris, Victoria, and Sappho were being discussed, it appeared that the residuals showed a period of about 27 days. This was traced to the lunar inequality of the Earth's motion round the Sun. Each month the Earth describes an orbit about the centre of gravity of the Earth The dimensions of this orbit are determinable from the and the Moon. inequalities in the positions of Victoria, Iris, and Sappho; and from the dimensions of the orbit the ratio of the masses of the Earth and Moon may be calculated. In this way Gill found for the mass of the Moon 1/81.60, a value confirmed by Mr. Hinks' discussion of the observations of Eros. Although not of the same importance as the solar parallax, this is a more difficult quantity to determine. The excellence of the determination of the positions of the stars which served as the reference points is the secret of Gill's success in this work. There was a thoroughness and completeness which made his research a model, and one which was, in fact, closely followed in the later Eros investigation.

The determination of the mass of Jupiter is a third important research made with the 7-inch heliometer. This was partly the observational work of Gill himself, and in part resulted from the younger astronomers whose enthusiasm he had kindled. Before Gill had taken up his appointment at the Cape, Adams had urged on him the need for observations to give the latitudes of the satellites of Jupiter, the longitudes alone being determined satisfactorily from eclipses. As it is not possible to obtain sufficient precision by measuring the positions of the satellites relatively to the planet, Gill adopted a method employed by Hermann Struve and obtained their positions relatively to one another. In 1891 he made a considerable series of observations and a smaller series was obtained by Finlay. The most interesting feature of this research is the care employed on the scale value of the heliometer, so that the observations might be employed to give the mass of Jupiter. A

pair of standard stars whose position-angle agreed nearly with the plane of the satellites was selected, and the scale value of the heliometer corrected by constant reference to these stars. Their absolute distance apart was derived by relating them to the Victoria triangulation, and found with a probable error of 1 in 100,000. The observations were not reduced till de Sitter's visit to the Cape, when he discussed them, and obtained a very accurate value for the mass of Jupiter, and also determined corrections to the positions of the planes of the four satellites. The subject was pursued further by Bryan Cookson, who visited the Cape in 1901-2 and again in 1905, and made a series of observations with the heliometer, while photographs were taken with the astrographic telescope. In this and subsequent work of de Sitter Gill took great interest, and was anxious that work on these satellites should The mass of Jupiter be continued with large photographic telescopes. found by de Sitter agreed closely with that derived by Newcomb from the perturbations produced in Saturn and the minor planets Themis and Polyhymnia by the action of Jupiter.

The introduction of the heliometer was a new departure in the history of Following the procedure established by Airy at the Cape Observatory. Greenwich, the work of the Observatory had till the time of Gill been mainly devoted to meridian observations. In consonance with the practical aim of being of service to navigation, Airy had made it his first business to determine the positions of Sun, Moon, planets and the brightest stars with all accuracy possible. This had resulted in a very full knowledge of the movements of the members of the Solar system and served as the basis of tables for the National Ephemerides. This work is of great importance, but the observations require to be carefully organised and constantly carried on. There is, however, no finality about it, and it tends to become of a somewhat routine character. By directing attention to other problems of Astronomy, and at the same time introducing a class of observations which demanded the greatest skill and care on the part of the observer, Gill gave new life to the Cape Observatory and new stimulus to British Astronomy. He did not, however, fail to recognise the importance of meridian work. He had in mind, from the time of his appointment, the improvement and development of Fundamental Astronomy. In particular, he desired to introduce a reversible transit circle, but this proposal did not meet with any encouragement from Airy and was postponed for a time. Observations with the non-reversible instrument were continued. A list of 303 fundamental stars, selected by his friend Prof. Anwers, were fully observed between 1879 and 1885, as well as Zodiacal stars, reference stars for heliometer and other observations, and stars which, in conjunction with observations at Greenwich, would serve to determine astronomical refraction. This formed the Cape Catalogue of 1713 Stars for the Epoch 1885. The stars observed between 1885 and 1895 were of a similar class; the results are contained in the Cape Catalogue of 3007 Stars for the Epoch 1890.

The next work with this instrument consisted in the observations of the

positions of 8560 stars between -41° and -51° declination, intended to serve as points of reference for the photographs, taken at the Cape, for the International Astrographic Survey. After this had been completed observations were begun towards a catalogue of Zodiacal stars, for use in heliometric and other observations in which the differential positions of the Moon or planets are obtained. For this work the co-operation of a number of other observatories was secured. Although the results of several of these observatories have been published, the co-ordination of the whole series of observations into a Standard Catalogue has not as yet been made.

During Gill's directorate the reduction and publication of Maclear's observations was completed. Maclear had left a large amount of valuable material with which he had been unable to reduce, but which his successors Stone and Gill have now discussed, thus giving the positions of a large number of southern stars at the middle of the nineteenth century.

While carrying out observations with the old transit circle, Gill kept constantly in mind his scheme for a new reversible transit circle, and steadily worked towards this end and lost no opportunity of advancing it. necessary expenditure was sanctioned in 1897, and Gill devoted his thought to the design and construction of an instrument which should be, as far as possible, free from the systematic errors which are the bane of Fundamental Astronomy. His great experience and his mechanical and engineering skill fitted him admirably for this difficult task. The difficulties which have to be faced arise from want of stability of the instrument, due to movements of the ground from changes caused by temperature in the atmosphere of the observing room and the positions of reading microscopes or the divisions of the circle, from uncertainties in the flexure of the telescope, and from personal errors inherent in the methods of observation. The instrument was designed so as to be reversible on its pivots, thus providing a check on the collimation, and with the eye-end and the object glass interchangeable, so that in the mean of the two positions the astronomical flexure should be eliminated. Temperature changes were minimised by making the instrument of iron or steel, which had a coefficient of expansion nearly equal to that of glass, and by carefully covering it with insulating material and so protecting it from the heat of the observer's body and other irregular radiations. The piers carrying the microscope were iron tanks containing water, so that constancy of temperature was preserved particularly in horizontal layers. But the most interesting and novel feature of this transit circle is found in the meridian marks. Permanent marks were obtained at depths of 30-40 feet in the Archaic rock. Marks on the surface vertically above these were determined optically on the principle of Bohnenberger's eyepiece, and this provided long focus collimators both north and south of the transit circle, by means of which its shift in azimuth may be readily determined at all times. This ingenious plan proved very successful and has been copied by several observatories. For the elimination of personal errors of the observer, he adopted the principle of the travelling wire, and developed the method of employing a

motor to make the wire move at approximately the rate of the star, the observer having only to keep the image bisected by means of slow motions. The instrument was not brought into full use till after Gill's retirement, but the excellent results which were obtained under his successor's direction were a source of great satisfaction to him. A remarkable proof of the value of the underground marks was shown by the detection of the movement of the Earth's pole in azimuth corresponding to the well-known variation of latitude.

In the development of stellar photography Gill took a considerable share. In 1882, the comet discovered by Mr. Finlay at the Cape Observatory was photographed by several people with ordinary cameras and without adequate means for following the diurnal motion. Gill strapped a camera with a 21-inch Dallmeyer lens of 11 inches focus on the counterpoise of an equatorial telescope, and obtained a series of photographs, interesting as representations of the comet, but specially remarkable for the large number of stars shown on the plate. The images were in excellent definition over a considerable field and the practicability of constructing star maps by photographic means was clearly indicated. Gill accordingly obtained from Mr. J. H. Dallmeyer a "rapid rectilinear lens" of 6 inches focus and 54 inches focal length, and, with the assistance of a grant from the Royal Society, commenced in February, 1885, a photographic survey of the southern sky. In December of the same year he received from Prof. Kapteyn, of Groningen, a proposal to undertake the measurement of these photographs and the formation of a 'Durchmusterung' or catalogue of the approximate positions and magnitudes of the stars. Gill welcomed this offer of co-operation very heartily. The methods to be pursued were discussed and the plates forwarded to Groningen. The work was completed most successfully by Kapteyn, who began the measurement in October, 1886, and completed it in February, 1898. The results are contained in three large volumes of the 'Annals of the Cape Observatory,' and comprise a complete survey of the southern sky between -18° declination and the South Pole. The positions and photographic magnitudes of more than 400,000 stars were determined: the Durchmusterung has been of the greatest service to astronomers in the southern hemisphere, and has served as a basis of important cosmical discussions by Kapteyn and others.

In December, 1882, Gill forwarded to Admiral Mouchez a short paper, for communication to the French Academy of Sciences, accompanied by photographs of Finlay's Comet, expressing his views on the practicability of charting the stars by means of photography. At this time Messrs. Paul and Prosper Henry, at the Paris Observatory, were engaged in charting the Zodiac. As they approached the Milky Way the difficulty of the task caused them to consider the possibility of employing photographic methods. Gill's communication came at an opportune moment, and they were encouraged by Admiral Mouchez to proceed with the construction of object glasses suitable for this purpose. Their constructive ability, combined with

the administrative skill of Mouchez and the persistence and enthusiasm of Gill, were the foundation of the great international enterprise for cataloguing and charting the whole sky by photographs on the large scale of 1 mm. to one minute of arc. From its inception in 1887 to the time of his death Gill assisted this scheme in many ways. He took an important share in the elaboration of the many details of the work itself, and in the correlated meridian observations necessary to give the photographs their greatest value. He clearly recognised that the 'International Photographic Catalogue' was a topographical survey which needed to be strongly connected with the principal triangulation furnished by meridian observations. In this and other particulars the conference held at Paris for the execution of the international chart and catalogue were largely guided by his views.

Gill's great power of getting a comprehensive scheme carried through is nowhere better shown than in the geodetic survey of South Africa. But for his influence it is probable that the different States of South Africa would have been content with small local surveys unconnected or at least very weakly connected with one another. Gill impressed on the Governments of the different States the value of an accurate survey based upon a principal triangulation of such high accuracy that it would be definitive for all future time. Very soon after his appointment at the Cape he outlined a scheme for a gridiron system of chains of principal triangulation extending over the Cape Colony, the Orange Free State, Natal, and the Transvaal. A commencement was made in 1883 by the decision of the Governments of Cape Colony and Natal to make a principal triangulation of these countries as a joint work. The observing in the field was placed under the direction of two officers of the Royal Engineers, Captain Morris (now Sir William Morris) and Lieutenant Laffan (now Colonel Laffan) who entered heartily into Gill's plans, and amidst difficulties carried out a survey of the highest The results of this work were published in vol. 1 of the precision. 'Geodetic Survey of South Africa' in 1896.

Gill saw that these operations might be made the commencement of a still more comprehensive work of the greatest geodetic importance. In his own words ('Geodetic Survey,' p. 157):

Looking forward to the practical and possible progress of geodesy, the question may be asked, Should not the progress made in geodetic survey in South Africa be regarded as the first step in a chain of triangulation which, approximately traversing the 30th meridian of east longitude, shall extend continuously to the mouth of the Nile? The amplitude of such an arc is 65°, and by triangulation through the Levant and the islands of Greece, it may be connected with the Roumanian and Russian arc, so as to form a chain 105° amplitude extending from Cape Agulhas to the North Cape.

This great project Gill kept constantly in mind and forwarded at every opportunity.

The next stage of the geodetic survey was in a different region. It became necessary to delimit part of the boundary between German and British South Africa, which had been fixed by treaty in 1890, as the

20th meridian, from the Orange River (latitude $28\frac{1}{2}^{\circ}$) to latitude 22° . It was arranged by Gill that the chain of triangles, which passed mainly through German territory in order to avoid the Kalihari desert, should start from Rietfontein, the northern limit of an excellent survey of South Bechuanaland by Mr. Bosman, and that the latter should be connected at its eastern and western ends with the surveys of the Cape and Natal. This was completed in 1899.

The interest of Mr. Cecil Rhodes was secured in the measurement of the great are along the 30th meridian, and in 1897 the Administrator of Rhodesia sanctioned the commencement. It was carried forward by Mr. Alexander Simms in Southern Rhodesia as far as the Zambesi. The outbreak of the war compelled a suspension of the work during 1902. In 1903 the work was continued by Dr. Rubin, under Gill's direction, and was carried forward by 1906 to within 70 miles of Lake Tanganyika, when it was suspended.

Soon after the close of the South African War the geodetic survey of the Transvaal and Orange River Colony was proceeded with. On Gill's advice Colonel Morris was put in charge of these operations, his own position being that of Scientific Adviser to the Governments of the two Colonies, so that unity of purpose might be preserved in these surveys and that they should form part of a harmonious whole. These surveys were completed by the beginning of 1906 and the chain on the 30th meridian was continued northwards as far as the Limpopo River. Thanks to Gill's efforts the survey party was kept together, and funds obtained, half from the British South Africa Company and half from scientific societies in England, which enabled the connection to be made with the chain in Southern Rhodesia. The great arc on the 30th meridian was thus carried from latitude 31° 36' to 9° 41'. As a result of these measurements, utilising 57 latitude stations, Dr. Bahn has shown that the terrestrial spheroid is somewhat greater than that of Clarke, in agreement with a determination by Hayford from the Geodetic Survey of North America.

When Gill went to the Cape in 1879, the Observatory staff was small, and the only instruments were the transit circle, a 7-inch equatorial, and a photoheliograph. The grounds, buildings, and water supply were in a very unsatisfactory state, and after heavy rains the road to the Observatory was nearly impassable, so that computers who were not in residence on the hill had to be carried there in carts. In consequence of Gill's persistent representations these things were gradually remedied, and sufficient provision made for the suitable maintenance of the grounds and buildings. The swamp at the bottom of the hill was drained, trees were planted, fences erected, buildings were repaired and extended, so that when Gill left, the Observatory and its surroundings were not unworthy of a scientific institution of its great importance.

To the instrumental equipment were added the reversible transit circle, the 7-inch heliometer and an astrographic equatorial, and the Victoria (24-inch) photographic refractor. The last of these instruments was a generous gift from Mr. Frank McClean, and was a tribute to Gill's great achievements

as an astronomer. Coupled with the 24-inch is an 18-inch visual refractor. Objective prisms and a powerful slit spectroscope were included in the gift. This munificent gift was intended to be in commemoration of Queen Victoria's Jubilee in 1897, and although the Observatory and telescope were not completed till a few years later, this date is inscribed on a tablet inserted in the front of the Observatory, which was unveiled by the Governor, Sir Walter Hely Hutchinson, in September, 1901. Valuable spectroscopic work has been done with the instrument. Gill was particularly delighted by the determination of the solar parallax from the changes in the apparent velocities of stars to or from the earth at different times of the year in consequence of the earth's orbital motion obtained from observations with the instrument by Dr. Halm under the direction of Mr. Hough.

The staff of the Observatory was increased in correspondence with the larger equipment, so that when Gill left the Cape the Observatory was qualified to carry out work of the highest order in many different directions, and was one of the finest Observatories in the world, and of additional importance from its situation in the southern hemisphere.

In 1905, the year before Gill left the Cape, the British Association visited South Africa. The invitation to the Cape was largely the result of Gill's efforts, and his unremitting labour as General Secretary contributed greatly to its success. He was delighted to welcome so many of his friends to South Africa, among others Sir George Darwin, Admiral Wharton, Dr. Backlund, Prof. Kapteyn and several younger astronomers from England and the Continent. The meeting in South Africa was signalised by Kapteyn's announcement of his discovery of star-streams.

Acting on his doctor's advice that a more bracing climate would be beneficial to him, Gill intimated to the Admiralty his desire to retire in February, 1907, after 28 years of service, and was granted leave of absence from October, 1906. He settled in London and was soon busily engaged in its scientific activities. He was President of the British Association at the Leicester meeting in 1907. He served on the Council of the Royal Society 1908-9, and again 1910-11; on that of the Royal Astronomical Society 1907-1913, being President 1910-12 and succeeding Huggins as Foreign Secretary in 1912; and on the Council of the Royal Geographical Society, 1908-10 and 1911-12. He also served on the Council of the British Science Guild, and succeeded Lord Cromer as President of the Research Defence Society. After he had settled in London a large part of his time was devoted to a History of the Cape Observatory with a full and technical description of the new instruments. This admirable work was happily completed and published a few months before his death. Gill thoroughly enjoyed the opportunities of seeing his many friends which his residence in London afforded him. He was constantly consulted by astronomers, particularly as to the design of instruments. His interests embraced not only the practical branches of Astronomy and Geodesy. with which his own work had been more particularly concerned. He followed with interest the current researches of astronomers in lunar theory, solar and

stellar spectroscopy, and especially those bearing on the extent and movements of the sidereal system. Another subject in which he was keenly interested was the manufacture of optical glass for large telescopes.

Nothing gave Gill greater pleasure than to invite his astronomical friends to his house, especially if an occasion was provided by the visit of a distinguished foreign astronomer, and to have a talk about Astronomy. He found a similar pleasure in the Astronomical conferences he attended, particularly those at Paris in connection with the International Photographic Chart of the Heavens and kindred subjects. These conferences were a source of great delight to him, because of the opportunities they furnished of personal intercourse with his friends, of finding out what they were doing, and how their work progressed, and in return telling them what he had in hand. They benefited by his advice and the results of experiences, but still more by the enthusiasm he communicated to them. Gill's influence is shown by the number of astronomers who worked in co-operation with him or were guided by him in their choice of work. Reference has already been made to Auwers, who undertook the discussion of the meridian observations in connection with the solar parallax, to Kapteyn's co-operation in the Photographic 'Durchmusterung,' and the parts taken by Elkin, Cookson, and de Sitter in heliometer and photographic observations. To these may be added Jacoby's work on the triangulation of the Victoria stars, and that of Innes on the revision of the Cape Photographic 'Durchmusterung.' spectra of the bright Southern Stars were obtained by him with the astrographic equatorial while he was a guest at the Cape. The valuable photographic survey of the sky made by Franklin-Adams was largely due to Gill's encouragement.

In the introduction to his 'History of the Cape Observatory,' Gill tells of the delight with which he read Struve's 'History of the Pulkova Observatory':

There is inspiration to be found in nearly every page of it, for its author had the true genius and spirit of the practical astronomer—the love of refined and precise methods of observation and the inventive and engineering capacity.

These words are as applicable to Gill as to Struve. He loved to make an instrument capable of the most refined measurements, and the pleasure of making observations as accurately as possible counterbalanced the tedium of making similar observations night after night. His force of character enabled him to triumph over difficulties and carry out great projects. His enthusiasm and tenacity of purpose communicated themselves to his colleagues and assistants, and his kindness of heart made them devoted to him.

Gill received many honours in recognition of his splendid services to Astronomy. He was created Companion of the Bath in 1896, and Knight Commander in 1900. He was created Commander of the Legion of Honour (France) in 1908, and Knight of the Prussian Order "Pour le Mérite" in 1910. He was an Hon. LL.D. of Aberdeen and Edinburgh, and Hon. D.Sc.

of Oxford, Cambridge, Dublin, and the Cape of Good Hope. He was elected a Corresponding Member of nearly all the Scientific Academies of Europe and America. The Gold Medal of the Royal Astronomical Society was awarded to him in 1882, and again in 1908; a Royal Medal of the Royal Society in 1903; the Valz Medal of the Institute of France in 1882; the Bruce Medal of the Astronomical Society of the Pacific in 1900, and the Watson Medal of the National Academy of the United States in 1900.

Since his return to London Gill's health had been excellent, and he thoroughly enjoyed an occasional day's golf or shooting. In December, 1913, he was suddenly seized with pneumonia, and passed away on January 24, 1914, after an illness of six weeks.

F. W. D.

G. W. HILL, 1838-1914.

GEORGE WILLIAM HILL was the son of John William Hill and Catherine Smith, and was born in New York City on March 3, 1838. Both his father and grandfather were artists, and he himself was of English and Huguenot descent. His early education, like that of most of the men of his time in America, gave him few advantages. In 1846, when his father moved from New York to the farm at West Nyack, the country was too busy with material development to produce many teachers who could give any but the most elementary instruction, and the country school which he attended must have been inferior in this respect to those of the larger cities. Even at Rutger's College in New Jersey, to which Hill was sent owing to the exhibition of unusual capacity and from which he took his degree in 1859, the course probably went but little beyond that now found in secondary There, however, he came under the influence of a man whose ideas on education were unusual. Dr. Strong, according to Hill's evidence, believed only in the classic treatises; but little published after 1840 was admitted to his library. Hill's sound knowledge of the fundamentals of his subject is doubtless due to this course of reading.

Hill's first paper, published in 1859 when he was but 21 years of age and before he had taken his degree at college, is a half-page note on the curve of a drawbridge. Two years later he showed his capacity in the essay which gained a prize offered by Runkle's 'Mathematical Monthly' for the best solution of a problem connected with the constitution of the Earth. President R. S. Woodward, who has himself worked much at this subject, says that the memoir is still worthy of careful reading.

In the year 1861 he joined the staff of the 'Nautical Almanac' office, which then had its headquarters in Cambridge, Mass., and for a year or two he worked there and thus had an opportunity for association with some of the ablest men of the time in astronomical science. But he soon obtained permission to do his work at the home in West Nyack which he never seemed to leave willingly during the rest of his life. It was there that nearly all his best work was done. In fact, he was only away from it for one considerable period, and this is covered by his residence in Washington from about the year 1882 until 1892; even during that time the summers were generally spent in West Nyack.

. In the first ten years after leaving college, Hill only published eight papers, and none of them deal with celestial mechanics in the modern sense of the term. But from his output after that time it is evident that he had been reading and digesting the newer treatises and memoirs as they appeared. Delaunay's two magnificent volumes on the lunar theory were published in 1860 and 1869 respectively, and the methods of that investigator exercised a fascination over Hill for the rest of his life. The other great lunar theorist of the period, P. A. Hansen, had been explaining his methods for many years before this time, and Hill was probably one of the few men of his time who understood them thoroughly. He does not seem to have been particularly drawn to them, although they are used in his theories of Jupiter and Saturn with but little alteration. It is difficult to find many traces of other influences in his work. His most celebrated memoir, it is true, is based on one of Euler's numerous methods, as he himself tells, but after the start he proceeds entirely on lines of his own devising.

The publications which follow his first attempts during this early period exhibit knowledge of theoretical astronomy and the power to handle large masses of numbers rather than any unusual mathematical ability. In his discussion of the observations of the great Comet of 1858, which was undertaken to obtain a satisfactory orbit (1867), he has to deal with 363 places gathered from many sources. As usual with Hill, he does not confine himself to the main point but discusses systematic errors between different observatories and those due to the size of telescope used. His final conclusion is that there is no evidence of any force other than gravitation influencing the motion of the comet.

It is probable that his work on this body was responsible for the next three papers: on the reduction of star places, the determination of the elements of a circular orbit, and the conversion of latitudes and longitudes into right ascensions and declinations, or, at any rate, that it drew his attention to these fundamental problems. But he was soon to lay them in the background for more original investigations in celestial mechanics proper. One can see in his published work the gradual approach to this subject. His tenth memoir is a correction to the elements of the orbit of Venus from observations extending over 33 years. It is followed by a

derivation of the mass of Jupiter from the perturbations of certain asteroids, and the calculation of an inequality of very long period in the motion of Saturn. Shortly before, however, he had been assisting in the campaign which had started some years earlier to get the utmost out of the transits of Venus in 1874 and 1882. Part II of the Papers of the United States Commission relating to the transits is by his hand: it consists of charts and tables for facilitating predictions of the several phases at any place on the globe.

The active period of Hill's work in celestial mechanics began in 1872. Between that year and 1877, when his two chief memoirs appeared, he published eleven papers on various phases of the subject, besides seven others in pure and applied mathematics and the long transit of Venus calculations already mentioned. Most of them are quite brief and call for no special mention.

In order that the value of Hill's contributions to celestial mechanics and more particularly to the lunar theory may be made clear, it is necessary to say a few words as to the condition of the subject at the time they were published. For 200 years mathematical astronomers, many of them of the first rank, had been devoting their energies to furnishing a complete demonstration of the power of the law of gravitation to account for the motions of all the bodies in the solar system within the degree of accuracy of the observations. In the third quarter of the nineteenth century it was evident that this demonstration would soon be made. Leverrier was publishing his tables for the positions of the great planets, while Hansen and Delaunay had completed their work on the Moon. For the purposes of navigation all needed accuracy had been obtained, and from the scientific side there seemed to be but few matters which needed explanation; the final polish which a few industrious workers might give was the last step. There was thus danger that the subject of celestial mechanics might encounter a blank The number of investigators began to dwindle. At the same time, pure mathematics and physics were showing vast territories to be explored, while the discovery of spectrum analysis and the use of the photographic plate attracted many astronomers who earlier would have devoted themselves to the mathematical side of the subject. From the old point of view this attitude on the part of astronomers was justifiable.

But Hill saw that there were problems other than the mere verification of the law of gravitation by comparisons of theory and observation of the chief bodies in the solar system, which would demand solution. He also saw, partly from the industrious work of Newcomb on the old and modern observations of the Moon, that even the enormous labours of Hansen and Delaunay on the theory of its motion would demand extension and verification if a test of the Newtonian law to the degree of accuracy of the observations were required. For the former object, a new set of problems must be formulated and a start made towards their solution; for the latter, a new method of procedure was practically necessary, for it was almost certain that no one

would repeat the calculations, which appeared to have been pushed as far as was humanly possible with the adopted methods. These two sides of Hill's work are quite distinct, even though they both start from the same memoir.

The older lunar theorists had taken the ellipse as a first approximation, that is, at the start the action of the sun was neglected. Hill proposed a first approximation in which a portion of the sun's action should be taken into account. If an examination of Delaunay's final expressions for the longitude, latitude, and parallax be made, it is seen that the infinite series proceed along powers of five parameters, and that the rate of convergence along powers of one of these, the ratio of the mean motions of the Sun and Moon, is far more slow than along powers of the others, owing to the presence of large numerical factors. Hill conceived the idea of neglecting all these other parameters and then finding the series in powers of this ratio alone, with all needed accuracy. He set up the equations of motion, solved them, and gave formulæ of recurrence which enabled him to avoid the slow approximation methods which generally advanced the degree of accuracy by only one or two powers of the ratio at each step; in his method it advances by four powers of this ratio. The expressions are worked out both literally and numerically, the latter being taken to fifteen significant figures, a number not very much in excess of what is actually required.

As obtained, the co-ordinates are referred to axes which move with the mean velocity of the Sun round the Earth, and in this form the expressions involve the time through its presence in multiples of a single angle. In the transformations which are necessary to convert rectangular co-ordinates to polars, Hill makes full use of the method of "special values" or, as it is now called, of harmonic analysis and synthesis. He was always very fond of this kind of transformation, using it much in later years and even attempting to systematise its use when many hundreds of terms were present.

It would be unjust in this connection not to mention the indebtedness of Hill to Leonard Euler, probably the greatest of lunar theorists since Newton. Euler, as Hill remarks, had had the idea of starting the theory in the same way with moving rectangular axes, and with the same first approximation, and had carried it out to a considerable extent in his theory published in 1772 and in a later memoir.

The further steps outlined by Euler, and quoted by Hill, consist of the determination, step by step, of the terms arranged in powers of the parameters which had been neglected. Each step is to consist of the complete calculation with all needed accuracy of the function of the time and the ratio of the mean motions which multiplies each combination of powers of the remaining parameters. There are several difficulties in following this process. The chief one, which Hill solved in the memoir on the perigee of the Moon, is the determination of the first new angle containing the time which arises in the second approximation. In later approximations this angle also involves all the parameters, and other methods are needed to find the new portions depending on them. Euler possibly foresaw this; Hill certainly did, but he

never carried his work to the degree of approximation which would need them. The method has been used by the writer for the construction of a complete theory of the Moon's motion.

The expressions for the co-ordinates, referred to the moving rectangular axes, have another property: they form Fourier series and are therefore periodic. The resulting orbit in this moving plane is consequently closed. Recognising this fact, Hill draws the curve. But he saw that the orbit was of interest apart from its application to the lunar problem, for he immediately proceeds to trace, with some care, orbits for values of the ratio of the mean motions other than that which holds for the actual Moon and Sun. He thus obtains a family of such orbits. It is Hill's idea of the periodic orbit which, developed chiefly by Poincaré and G. H. Darwin, has given new life to the whole subject of celestial mechanics and has induced many mathematicians to investigate on these lines. The treatise of the former, 'Les Nouvelles Méthodes de la Mécanique Céleste,' is based mainly on the idea. Darwin actually traced many such orbits under varying conditions.

There is still another portion of this memoir which has been largely used as a foundation for investigations into the stability of celestial systems. If the eccentricity of the Earth's orbit round the Sun be neglected, it is possible to write the relative energy equation in a finite form. Referred to the same moving axes, the square of the velocity can, in fact, be expressed as a finite algebraic function of the co-ordinates. Since the square of the velocity can never be negative, this function, equated to zero, gives the equation to a surface which the Moon cannot cross. As the surface consists of various ovals and folds, we can obtain certain limitations on the path of the Moon and therefore carry forward the question of the stability of its motion one important step. Hill draws the surfaces for a limited case. Darwin made extensive use of a similar diagram for a more extended case, and many others have followed on the same lines.

Thus this memoir, of but 50 quarto pages, has become fundamental for the development of celestial mechanics in three different directions. Poincaré's remark that in it we may perceive the germ of all the progress which has been made in celestial mechanics since its publication is doubtless fully justified. It has sometimes been said that Hill did not appreciate at the time the importance of his work. Hill was far too modest about his own achievements to lay any such stress on his productions as has the scientific world. But it does not require an extended study of his memoirs to see that his vision often went beyond the particular matter in hand.

The second memoir of 1877, On the Part of the Motion of the Lunar Perigee which is a Function of the Mean Motions of the Sun and Moon, has already been referred to. It is essentially a continuation of that part of the researches which deals directly with the lunar problem, although published a few months earlier. While not so far-reaching from the point of view of future developments, it is even more remarkable as an exhibition of Hill's powers of analysis. In it, the determinant with an

infinite number of elements is raised from a nebulous possibility to an instrument of computation. Hill's periodic orbit contained only two of the four arbitrary constants which the complete solution of his differential equations requires. He, therefore, proceeds to find an orbit—no longer periodic—differing slightly from the periodic orbit but still satisfying the differential equations to the first power of the small variation. The equations obtained are two of the second order and linear with respect to the two unknown dependent variables. An able analysis with the use of known integrals enables him to reduce the solution to that of one of the second order in the normal form—

$$\frac{d^2p}{dt^2} + \nabla p = 0,$$

where V is a known Fourier series depending on the time. Knowing the form of the solution—

$$p = \sum a_i \cos \{c(t-t_1) + 2i(n-n')(t-t_0)\}\$$

from previous work in the lunar theory and which he justifies by general considerations, Hill substitutes and obtains an infinite series of linear equations for the determination of the unknowns a_i . But c is also unknown and it does not enter in a linear form. The a_i are eliminated by means of a determinant with an infinite number of rows and columns equated to zero; this is therefore a determinantal equation to find c, the main object of the investigation.

Then follows a remarkable series of operations. The determinant is reduced to a convergent form (though it was left to Poincaré to furnish the proof of convergence) by dividing each row by a suitable factor which reduced every element of the principal diagonal to unity. Next, the unknown, c, must be isolated; Hill achieves this by recognising that if c be a root so must c+2ibe also a root and that, therefore, all the roots can be expressed by a cosine function. On the assumption that there are no other roots, he equates the determinant to the cosine function, obtaining the constant by comparing the highest (infinite!) power of c on each side of the equation. A particular value of c (not a root) can be inserted in the identity thus obtained. In this way, Hill reduced the work to a computation of an infinite determinant every element of which is known. He gives a general method for this expansion which enables him to tell at once the order of the terms neglected when the series is cut off at any place. Each term of this series, however, consists of singly, doubly, ..., infinite series which must be summed. The labour at this stage was very great and it caused a corresponding liability to error. Hill carried it through with complete success in its general form, afterwards substituting numbers and determining c to 16 significant figures. principal part of the motion of the Moon's perigee is immediately deducible from c. President Woodward relates that the determinant was solved during one of two trips which Hill made to the north-west region of Canada; I imagine, however, that this statement refers to the method to be adopted rather than to the actual computation.

The story of these two memoirs is incomplete without a notice of the work of J. C. Adams on somewhat similar lines. Almost immediately after their publication, a brief paper by him appeared in the 'Monthly Notices' of the Royal Astronomical Society. He had also taken up Euler's idea and had obtained the variation orbit as a first approximation. But he turned to the motion of the node instead of to that of the perigee. The investigation here follows lines very similar to those of Hill, the solution of the infinite determinant being closely analogous.

It is convenient at this stage to take up Hill's work rather by subject than in chronological order. The periodic orbit used with such excellent results in the lunar theory is tried later (1887) on the motion of the satellite Hyperion as disturbed by Titan and the results applied in a following paper to obtain the mass of the latter. These were written before the publication of Poincaré's researches. Only on one occasion did he make it the subject of a theoretical research, and it was then probably stimulated by reading Poincaré's 'Mécanique Céleste.' As the title, 'Illustrations of Periodic Solutions in the Problem of Three Bodies,' indicates, it consists of applications to certain bodies in the solar system.

From time to time a paper was published advancing the applications to the lunar theory. In one, the periodic orbit is extended so as to include the terms which depend on the ratio of the parallaxes of the Sun and Moon as well as on the ratio of the mean motions. In another the terms dependent on the latter ratio and on the first power of the solar eccentricity are computed. In still another paper he calculates the expression for the principal part of the motion of the moon's perigee as far as m¹¹ literally in order to settle the correctness of Delaunay's value, which had been questioned as to certain of the earlier powers of m by Andoyer. Beyond these, he seems to have made no effort to continue the work in this direction. Possibly this was due to the heavy labour on the theories of Jupiter and Saturn which engaged him at least until 1892. In fact, as early as 1888 he stated in a letter to Sir George Darwin that he scarcely expected to proceed with the subject.

His fondness for Delaunay's methods has already been mentioned. One of his most valuable memoirs is an application of them to the calculation of the smaller perturbations of the Moon's motion which arise from the action of the planets and the figure of the Earth. Hill, using Delaunay's methods and results, showed, in a short paper on the Jovian evection, that the whole action of the Earth and Sun on the Moon could be treated as known from the start, and that therefore only one approximation was needed in order to get the effect of any disturbance whose square could be neglected. All later investigators have used this method. The formulæ of Delaunay are literal, while Hill's final equations for the calculation of the effect of any small disturbing force have the great advantage of well-determined numerical coefficients to be multiplied by the constants which depend solely on the nature of the given force.

In an earlier paper he had also shown how the disturbing function for direct planetary action can be expressed as a series of products, one factor in each product containing the co-ordinates of the Earth and Moon only, while the other contained those of the Earth and planet only. The former could, therefore, be computed once for all; it was the latter which required separate computations for each planet. This paper has also formed the basis for all the complete calculations of the planetary disturbing forces which have been made since its publication in 1883.

But Hill's most extensive application of Delaunay's theory is made in its original form to the calculation of the inequalities produced by the figure of the Earth. While he carried these to the degree of accuracy needed for observation, the method appears to be somewhat long and complicated. has to be applied in a literal form, and this requires expansions which converge very slowly. As a matter of fact, a few days' work with the methods which he adopted for the planetary terms will furnish the inequalities with all needed accuracy. In the first part of this paper Hill, not content with the values for the flattening of the Earth which were then in use, deduced one directly from a large number of pendulum observations all over the Earth. The result, 1/288, is considerably larger than most of the other determinations, and notably so than that of Helmert, 1/298, deduced from the same class of observations. The memoir occupies over 140 pages, and must have demanded an enormous amount of careful and accurate algebraic computation. complete the account of his work on the lunar theory, mention must be made of his calculation, by de Pontécoulant's method, of the principal inequalities produced by the motion of the ecliptic. Hansen was the only writer who had found the term in longitude as well as in latitude, and nearly all his calculations of the small perturbations are doubtful. Hill, of course, obtained correct results as far as he went in the matter.

Newcomb, who had taken charge of the American Ephemeris in 1877, soon induced Hill to undertake the theories of Jupiter and Saturn, and so give material assistance in his plan of forming new tables of the planets. The method adopted is that of Hansen with only a slight modification, which consisted in expressing the computations directly in terms of the time instead of using two auxiliary angles. That he used an old method in preference to devising a new one is perhaps unfortunate, even though the result leaves little to be desired. Had he taken more time over the preliminary stages we should probably have had something new and original, for Hill was then at the height of his powers as a mathematician. But he was doubtless under some pressure from Newcomb, who wished to complete his great plan during his tenancy of the office of director, and Hill himself may have desired to finish the calculations as soon as possible in order that he might return to West Nyack. However this may be, he completed the task successfully, as may be judged from the small residuals which he obtains after a comparison with observations extending over 150 years. The Tables which he formed from the theories of the two planets are now used in most of the national ephemerides. In 1882, Hill published a memoir of some length on Gauss's method for computing the secular perturbations of the planets. Gauss had outlined only the general idea. Hill takes it up and develops in detail the formulæ to be used. In the course of the work he finds that a considerable portion of the calculation depends on three elliptic integrals which may be needed for values of the argument up to 50°. Consequently, a large part of the paper consists of the tabulation of these to eight places of decimals at intervals of a tenth of a degree; the first and second differences are also printed so that the Tables are in form ready for interpolation. As an example, he computed the secular perturbations of Mercury by Venus with great accuracy. Two further papers on the same subject appeared in 1901.

In these years Hill published a number of short papers in the 'Analyst,' a journal no longer in existence. Sometimes they are merely solutions of well-known problems, at other times simplifications of proofs of theorems which had evidently presented difficulties to him and which he felt needed elucidation or elaboration—two favourite words with him. But Hill was not a great expositor: even for those familiar with the subject his work is often difficult and sometimes obscure. Newcomb used to say that if Hill had only the faculty of explaining his own ideas he might have avoided many an error and saved much time. Hill's ability to assimilate and extend the work of his predecessors, at any rate in his earlier days, doubtless prevented him from appreciating the difficulties of others. When the reader is used to Hill's style of composition and his general plans in writing out what he had to say, his arguments are much more easily grasped, but he is rarely anything else than concise.

In his last years Hill still continued to publish, in spite of failing health. He covered a variety of topics, several of them quite away from the region of celestial mechanics. One of the most extensive of his papers is a memoir on dynamic geodesy, the last in the fourth volume of his collected works and not previously published elsewhere. Some later papers on a variety of subjects will appear in a fifth volume, to be published, like the previous four volumes, by the Carnegie Institution of Washington.

If an attempt is made to regard Hill's work as a whole and to try to find out his point of view, one thing stands out clearly: a desire to obtain exact knowledge about natural phenomena, in however limited a field, which could be expressed in a numerical form. He never seemed to hesitate about making long calculations, and apparently had a positive liking for obtaining his results to many places of decimals. But, unlike the tendencies of those who engage much in computation, his mind did not seem to get cramped by figures. Not only could he see both trees and wood, to adopt a familiar simile, but could trace paths in the wood and keep his eyes open for roads which led in directions other than that he was exploring. He had remarkable ability for algebraic manipulation, which reached its highest manifestation in the memoir on the perigee of the moon. The more modern sides of mathematics appealed to him but little; if a formula or a series could be

reduced to numbers, such questions as convergence did not trouble him much, a point of view which has later been fully justified by Poincaré. He seemed to take but little colour from the work of others. Even when, as in many cases, he starts with the results of some previous investigator, his writing shows but little influence of the source of his ideas; it is individual and carries the reflection and methods of his own mind.

Hill never married. He lived much alone, but while resident in Washington would take long walks on Sunday, often with one or two companions. He was fond of botany without being a collector of specimens and found his chief outdoor recreation in the study of nature. He made two long canoe trips in the north-west of Canada. A carefully written diary, illustrated with photographs of the second expedition, which took him by rivers and lakes from Lake Superior to Hudson's Bay, is amongst the books which he left in his will to Columbia University.

He was President of the American Mathematical Society from 1894 to 1896 and served as lecturer on celestial mechanics in Columbia University from 1898 to 1901. The manuscript of his lectures shows that they must have cost him much labour; it contains long algebraic developments and is apparently intended to be a more or less complete account of the methods by which the motions of the Moon and planets are calculated. His numerous honours include foreign membership in the Royal Society, the Paris Academy, and the Belgian Academy. He received the Schubert Prize (Petrograd), the Damoiseau Prize (Paris), and the Gold Medal of the Royal Astronomical Society. He was elected to foreign membership in our Society in 1902, and received the Copley Medal in 1909.

His chief characteristic was a single-minded devotion to the subject which he had made his own. A highly sensitive conscience was always apparent in his dealings with the world: he refused to accept the salary of his lectureship at Columbia one year because no students then appeared to attend the course, and this in spite of the fact that the endowment allowed him absolute freedom to lecture or not as he chose. In later years he rarely left West Nyack, owing to ill-health. He died on April 16, 1914, from heart failure, and was buried near the graves of his ancestors not far from his home.

E. W. B.

SIR GEORGE NARES, K.C.B., F.R.S., 1831—1915.

In the death of Admiral Sir George Nares our Society has to regret the loss of a very meritorious scientific officer who had been a Fellow for nearly 40 years.

George Strong Nares came of a literary family, among its members being Archdeacon Nares, the author of the best life of Lord Burleigh. Born in 1831, young Nares entered the Navy in 1845, and served first on board the "Canopus," when he saw some feats of seamanship in the Tagus, in the exchange of main yards with the "Asia" flagship, bound for the Pacific. His next service was on board the "Havannah" in the Pacific, when his scientific training was commenced. Nares was appointed to the "Resolute," under Captain Kellett, in the Arctic Expedition of 1852 to 1854. He commanded the auxiliary sledge to Lieutenant Mecham, who, next to McClintock, was the greatest of Arctic sledge travellers. Nares performed this service admirably, going as far as Eglinton Island, where he made a collection of fossil wood, a most interesting geological discovery. On his return from Arctic service he was promoted to the rank of Lieutenant.

For the next ten years Nares was most usefully employed in surveying and in the work of instruction. In the "Illustrious" he was in charge of the training of cadets, again in the "Britannia," and he had the "Boscawen" training ship. He wrote by far the best book on seamanship since the days of Darcy Lever, which went through several editions, and was translated into French and Italian. As a surveyor, in command of the "Salamander" and "Shearwater," he surveyed Torres Strait, part of the coast of Australia, and the Gulf of Suez with reference to the construction of the canal. But his best known and most important surveying work was on board the "Challenger" in the expedition which was due to the representations of the Royal Society. His labours extended over the Atlantic, Indian Ocean, and as far as the Antarctic regions, where he discovered what appeared to be an opening which still remains to be explored. Narcs was recalled from the "Challenger" to take command of a scientific Arctic Expedition, due to the strong representations of the Royal and Royal Geographical Societies. The Societies desired discovery and scientific research, the Admiralty an attempt to go as near the Pole as possible. The Smith Sound route was selected as the best for discovery and scientific research, and Nares showed consummate seamanship in forcing the "Alert" through the ice to 82° 27' N. The results of the expedition were most valuable. Commander (now Admiral Sir Albert) Markham, in his memorable sledge journey, reached a latitude of 83° 10′ 30″ N. The northern coasts of Grant Land and Greenland were discovered for a distance of 300 miles. A fossil flora of extraordinary interest was one great geological result, and the geology and biology of the region were carefully examined through the ability and inexhaustible energy of Colonel Feilden, the naturalist of the expedition. Captain Nares himself conducted the astronomical, meteorological, magnetic, and tidal observations. The tides then observed proved the insularity of Greenland.

An outbreak of scurvy made it necessary for the expedition to return after the first winter; but it had done excellent work and more than justified the exertions of the Royal Society in procuring its despatch. Captain Nares was created K.C.B. for this great service.

Sir George Nares again commissioned the "Alert" in July, 1878, and was engaged in revising and extending the survey of Magellan's Strait until March, 1879. He returned, to take up the responsible post of Professional Officer in the Harbour Department of the Board of Trade, which he held for 17 years. He was then for four years Conservator of the Mersey. Indeed Sir George Nares was in harness, in the service of his country, for a good deal over 60 years.

The enumeration of the work he did is sufficient to establish the position of Sir George Nares as a distinguished scientific officer. He was a most amiable, kind-hearted man. Those who were under his instruction always speak of him in terms of affectionate regard, and he was beloved by the officers of the Arctic Expedition.

Admiral Sir George Nares died, in his 84th year, on January 15, 1915, and the funeral took place at Long Ditton. The body of their beloved chief was followed to the grave by six of his old Arctic officers.

C. R. M.

SIR JOHN MURRAY, K.C.B., 1841-1914.*

SIR JOHN MURRAY was born on March 3, 1841, at Coburg, Ontario. He came of one of those Scottish families that have done so much for Canada, and, indeed, throughout his life no one would have mistaken him for anything but a Scot. His father, Robert Murray, an accountant, had left Scotland seven years before and settled in Upper Canada, where during the troublous times of the Mackenzie Rebellion he took an active part in Canadian politics. John was for a time at the Public School of London, Ontario, and later at Victoria College, Coburg. When he was seventeen years old he left Canada and, as he has himself reminded us, he then for the first time saw the sea whose problems he was destined to make his own. When he left that early home, he says, "to find another amongst my relatives in Scotland, I had not yet seen the ocean. The voyage across the Atlantic made a great impression on me, so different was the salt, rolling sea from the great fresh-water lakes with which I had up to that time been familiar, and I was fascinated by the operations of the officers on the bridge when taking the altitude of the sun at each mid-day." On witnessing the rise and fall of the tide for the first time on the West Coast of Scotland, the impression was still more profound.

John Murray found a new home amongst his Scottish relatives, one of whom was John Macfarlane, his maternal grandfather at Coneyhill, Stirlingshire. He helped his grandfather in purchasing and collecting specimens for a museum, the remnants of which are still exhibited in the Macfarlane Institute at Bridge of Allan, many of the labels being in Murray's handwriting. Whilst living with his Scottish relatives he attended the High School, Stirling, and here he showed great interest in science. He used to pay especial attention to the teaching of Mr. Duncan Macdougall, from whom he learnt the principles of the sextant and how to construct an electric lamp and a battery of 80 Bunsen cells.

Murray remained for a long time at School and College. In fact, as he himself records, he came to be known as a "chronic student" at the University of Edinburgh. One thing he would not do, he would not go infor examinations. He learnt what he wanted to learn, and the mere learning was to him its own reward.

At the University, although in the main he followed the Science course, he was not infrequently to be seen in the lecture rooms of the literary professors and from time to time in those of the theological professors. Amongst his student friends more than one have made a mark on the theological thought of the last half of the nineteenth century. Occasionally

^{*} In writing this short memoir of my friend I have been greatly helped by Mr. Laurence Pullar, of Bridge of Allan and Bridge of Earn, by Dr. Hugh Robert Mill, by Dr. J. Sutherland Black and by Mr. James Chumley, who for many years was Sir John Murray's chief assistant.

he even listened to Law. His Zoology and Anatomy he studied under Goodsir and Turner, the present Principal, whilst he worked at Chemistry with Playfair and Crum Brown, and at Natural History with Allman. But undoubtedly the teacher who made most mark upon his mind was Prof. Tait, in whose laboratory he worked for several terms under William Thomson (afterwards Lord Kelvin), Clerk Maxwell, and with his life-long friend, Robertson Smith, who at that time was Demonstrator to Tait and was writing more than one mathematical paper of note. Later Robertson Smith became a distinguished Semitic scholar, one of the editors of the 9th edition of the 'Encyclopædia Britannica,' and after a theological controversy with the Free Church of Scotland a Professor of Arabic in the University of Cambridge, and, finally, University Librarian.

Tait was then, perhaps, at the height of his reputation and many students of various sorts were attracted to his laboratory; Sir John Jackson and Mr. Meik, the celebrated engineers, were amongst the young physicists, and curiously enough Robert Louis Stevenson was another. The last named, however, had no interest in science and used to beguile his demonstrator, Robertson Smith, into theological disputes, so dear to all true Scots.

Murray was always a great individualist, and he worked at what interested him with no eye to examinations or degrees, and although in later life he must have been surfeited with honorary degrees, as a student he passed by the examinations and the consequent degrees and never graduated.

In the year 1868, in a spirit of adventure and on the strength of having attended medical classes in Edinburgh, Murray accepted the post of surgeon on the whaler "Jan Mayen." He left Peterhead in February, and was away seven months. He saw a good deal of the Arctic regions, explored part of Spitzbergen, and landed at least once on Jan Mayen. During his absence his grandfather died, and Murray arrived home two days after the funeral to find that—unlike Loudon Dodd—he had been cut out of his grandfather's will with less than the proverbial shilling. It was the experience he gained on this Arctic voyage and during his subsequent work on the West Coast of Scotland in the years 1869 and 1870 which qualified him for his next post.

Murray's great chance in life came when the Government decided, on the recommendation of the Royal Society, to equip a surveying ship, the "Challenger," for scientific research and to send her round the world. "The 'Challenger' was a spar-decked corvette of 2306 tons, with auxiliary steam to 1234 horse-power," and was well adapted for the scientific purposes to which she was devoted for four years. The scientific staff was under the direction of Prof. (afterwards Sir) Wyville Thomson, of Edinburgh University, and at first John Murray was not included on it; but at the last moment, owing to the failure of one who had been chosen, on the earnest advice of Prof. Tait, John Murray was selected for the vacant post. This especially dwelt upon the fact of Murray's resourcefulness and readiness, and considered he would be a very useful man to have at hand in case of any difficulties

with natives or other possible sources of trouble. It was characteristic of Murray to embark on such an enterprise at a moment's notice, when there was almost no time to get together his scientific or personal "kit."

But the science of the depths of the sea and the science of oceanography were in these times inchoate. The first great expedition to investigate the physical, the chemical, the geological, and the biological conditions of the great ocean basins was sent out in 1872 by the Government of this country, then under Mr. Gladstone, and in that year H.M.S. "Challenger" left England with a staff of scientific observers to traverse the salt waters of the globe. From that date until the present time no such complete and organised a staff of scientific observers, helped in every way by the naval officers (for it was an Admiralty Expedition), has left any country for so prolonged and exhaustive an investigation into the economics of the ocean. The "Challenger" Expedition set a standard—in fact it practically established a new science, a science of which Sir John Murray was, in a way, the arch-priest.

The "Challenger" Expedition had predecessors, though on a much smaller scale. Maury had done a great deal in the way of the study of the ocean, especially in so far as concerned its depth and the ocean currents. Dr. Wallich on H.M.S. "Bulldog," surveying the route for the proposed Transatlantic cable, added much to our knowledge, and there were others. The immediate precursors of the expedition of the "Challenger" were a series of voyages made by the "Porcupine" and "Lightning" under the scientific guidance of Dr. W. B. Carpenter, Mr. Gwyn Jeffries, and Prof. Wyville Thomson. Dr. W. B. Carpenter took an immense interest in the question of deep-sea temperatures, and read a number of papers to the Royal Society dealing with all existing data accumulated down to 1870, and he was one of the leading spirits in stirring up that Society to urge the Admiralty to undertake the "Challenger" Expedition. At the Admiralty they were aided by the then hydrographer, Admiral G. H. Richards, who was extremely sympathetic with the work.

As the introduction to the narrative of "The Cruise of the 'Challenger'" recites: "The vast ocean lay scientifically unexplored. All the efforts of the previous decade had been directed to the strips of water round the coast, and to enclosed or partially enclosed seas. Great things had certainly been done there, but certainly far greater things remained to be done beyond. This consideration led to the conception of the idea of a great exploring expedition which should circumnavigate the globe, and, if possible, find out the conditions of life at the surface of the sea, at the intermediate depths, and also at the profound abysses of the ocean. Sir John Murray's main interest in the expedition was at first physical and geological rather than biological, though he soon acquired a real knowledge of animals, at any rate in so far as they affected the problems which appealed more nearly to him." He was an adept at criticising machines and instruments which plumb the secrets of the deep, and as soon as the results of his researches on the

bottom of the deep sea had appeared he was recognised at once, and as long as he lived, as the authority on the deposits covering the floor of the ocean.

Sir John was no specialist. He had ever the widest point of view of the chemistry, the physics, the geology, and the biology of the ocean, and to him these varying sciences always had their full value in the problem which he had made his own. He was constantly devising new sounding apparatus for bringing up samples of the sea bottom, thermometers for testing the bottom temperature, instruments for registering the pressure at great depths, and other implements which have made our knowledge of the depths of the sea accurate and even minute.

The ship sailed from England, quite at the end of 1872, with John Murray on board as Naturalist at a salary of £200 per annum. From the time of its departure Murray gave especial attention to the various oozes and other deposits which compose the floor of the ocean, and at an early period he came to the conclusion that Bailey, Johannes Müller, Count Pourtalès, Krohn, Max Schultze and Ernst Haeckel were right when they attributed certain of the minute shells at the bottom of the ocean to organisms which live nearer the surface. Murray correlated the contents of the surface tow-net with the results of soundings and found a close relation to exist between the surface fauna of any locality and the deposit which lies beneath it. Amongst other organisms he paid much attention to the curious coccospheres and rhabdospheres, as Murray now for the first time called them. He devised an ingenious method of abstracting these extremely minute organisms from the sea-water by stretching pieces of fine thread through a bucket of salt water and allowing it to stand for the night. The examination of the threads next morning showed these organisms entangled among the strands. Another unfailing source of supply of these curious, and still imperfectly understood, organisms was the stomachs of the Salps, whose pharynx, fine as its walls are, allowed these organisms to pass through its narrow-meshed sieve.

'The "Challenger" Report on Deep-Sea Deposits' by Murray and Renard was published in 1891. It was the first attempt to deal with marine deposits as a whole, and became at once the standard book on this subject, a position it occupies to the present day. It was in every sense of the word "epochmaking." The amount of research work entailed in the preparation of this monograph was stupendous; the detailed microscopic study and chemical examination of thousands of deposit-samples from all parts of the world and from all depths, and of the various constituents contained therein, involved the expenditure of much time and labour.

The terms applied to the various types of deposits, with the exception of "Globigerina coze," already in use before the time of the "Challenger" Expedition, were devised by Murray on board the "Challenger," some of them being subsequently more or less modified in collaboration with Renard. The nomenclature and classification finally adopted by them have stood the test of time. Notwithstanding the numerous contributions to the subject published in the interval, and the many attempts to improve upon either the divisions,

the terms, or the methods originally employed, the "Challenger" Report remains the model and standard upon which all studies of deep-sea deposits are based, and it appears to satisfy all the demands made upon it. This is conclusive evidence of the abundant foresight, care, and scientific precision brought to bear upon the study of the "Challenger" material and of material collected by other ships up to the time of publication.

Murray came to be recognised as the authority on all matters relating to the floor of the ocean. His reputation became world-wide, and his advice was solicited on all hands in connection with the fitting out of expeditions and with the scope of deep-sea researches of various kinds. Needless to say his extensive knowledge and practical experience were freely placed at the service of scientists, and many further additions to our knowledge of the sea and its laws are due to his initiative.

The bottom samples collected by nearly all the surveying ships, cable ships, and oceanographic expeditions of all nations, found their way to the "Challenger" Office in Edinburgh for examination and report, and Murray was thus enabled to bring together a magnificent collection of marine deposits, a collection which is unique in the world.

One may quote here an appreciation of his work given by the well-known Arctic explorer, General Greely. Writing two years ago in the 'National Geographic Magazine of Washington, U.S.A.,' General Greely says: "Nearly 40 years since, a distinguished scientist, born on the continent of North America, Sir John Murray, of 'Challenger' Expedition and fame, and one of the eight honorary members of the National Geographic Society, considered the mooted extent of South Polar lands and finally outlined their logical continental form as the continent of Antarctica—a fitting and largely accepted name. This great feat of constructive geography depended on a few score handfuls of oceanic ooze from the South Polar seas and scanty bits of rocks from scattered lands. Whatever doubts remained as to the accuracy of Murray's deductions have disappeared since the cumulative discoveries of Amundsen, Borchgrevink, Bruce, Drygalski, Gerlache, Larsen, Nordenskiöld, Scott and Shackleton."

Secondly, Sir John did much to throw light upon the origin of coral reefs. At the time of the "Challenger" Expedition Darwin's theory of subsidence held the field, but Murray, who proved all things and held fast only to that which he conceived to be true, found occasion to doubt its universal application. The boring at Funafuti, an island which was especially selected alike by the opponents and adherents of Darwin and Murray respectively as a typical place for investigation, clearly proved that Darwin was right in some places; there is room enough in the world for some coral islands to have been formed by sinking and others by the rising of the earth's crust. Darwin himself always admitted, after the publication of Semper's memoir, that his subsidence theory was not of universal application.

At the time of Murray's return from the "Challenger" Expedition, Sir Archibald Geikie, O.M., was Professor of Geology at the University of

Edinburgh, and Murray then attended his lectures. Sir Archibald helped him in the preparation of the geological section of the "Challenger" Reports and Murray took an active part in the many excursions which are ever the delight of the geological student. Sir Archibald has kindly written the following lines:—

"During the preparation of the geological parts of the 'Challenger' Reports we had long talks over the problems suggested by the observations made on the voyage. He was always an original and suggestive thinker in connection with these problems. Nowhere are his originality and acuteness more conspicuous than in his discussion of the origin of Up to this time, Darwin's explanation held the field, coral reefs. though a few observers had challenged its universal application. But when Murray published his views, in which he combated the proofs of vast oceanic subsidence and held that all the types of coral reef could be accounted for without subsidence and even with local elevation, he effected one of the most striking revolutions in geological theory which have taken place in our time. When Alexander Agassiz took up the question and made a prolonged series of expeditions over the coral regions of the oceans he brought a vast mass of fresh material in support of Murray's opinions. While I think it quite possible that here and there Darwin's explanation may be found to hold, I feel tolerably certain, after Agassiz's ample succession of explorations, that Murray is right for the general origin of coral reefs over the globe.

"Then Murray's laborious researches into the nature and distribution of the materials that are accumulating on the ocean floor and his classification of them broke entirely new ground in the Dynamical section of Geology. Many a long discussion he, Renard, and I had on this subject, and it was a delightful experience to watch how, bit by bit, out of the vast mass of materials collected by the 'Challenger,' there emerged the clear and impressive generalisations which were embodied in the 'Deep Sea Deposits.' Murray and Renard, by this remarkable volume, rendered a noble service to Oceanography and to our knowledge of the geological processes now in action in the oceans.

"Murray's later work on the Scottish lakes is another example of his originality and thoroughness. He not only planned this work with great skill and wide knowledge but, as it proceeded, he threw into the labours of his associates much of his own enthusiasm and devotion."

During the time that Murray was seeing the "Challenger" Reports through the press he was engaged with his friend, the late Mr. Robert Irviue, and others, on a series of chemical investigations upon the secretion of carbonate of lime from sea-water by marine organisms and on the part played in this process by the waste products given off during their nutrition. He also worked at the bacteriology of the deep-sea deposits, developing the work of the Russian oceanographers on the sulphuretted hydrogen bacteria of the

Black Sea. The series of papers recording these researches appeared in the 'Proceedings' of the Royal Society of Edinburgh.

The third investigation, referred to by Sir Archibald, on which he embarked in his latter years was that of the bathymetric survey of the freshwater locks of Scotland. The Councils of the Royal Societies of London and of Edinburgh had urged the Government to undertake this survey. The Government did not feel that this enterprise came within the province of the Ordnance Survey Office nor within that of the Hydrographic Department of the Admiralty, but when Murray wanted a thing done, in the long run it generally was done, and he and Mr. Frederick Pullar in 1896 commenced the work and had already published some papers of importance when by the accidental death of Mr. Frederick Pullar by an ice accident in 1901, the work His father, however, Mr. Laurence Pullar, determined to was interrupted. see the work through, and provided a large part of the funds used for this purpose, and in 1902 a staff of assistants was appointed to resume the survey. For the next four years the surveying work was vigorously carried on, and some 60,000 soundings were recorded from no less than 562 inland lakes. Biological and physical observations were also carried on during the two following years, and the results of this, the most careful survey ever carried out on the inland waters of any country, were published in six handsome volumes in 1910.

One would have thought that three such problems as Deep-Sea Deposits, the Origin of Coral Islands, and the Fresh-Water Lochs of Scotland, would have exhausted the energies of any man, but Sir John seems to have been tireless in his activity. Besides editing the 50 volumes of the "Challenger" Reports, he was the author of the summary of the scientific results of the expedition in two large volumes. As he records, "The direction of the whole of the work connected with the publication of the scientific results passed unexpectedly into my hands, and I have done my best under the circumstances to place on permanent record a trustworthy account of the labours of this famous expedition. It has been my earnest endeavour to complete the publication in a manner worthy of the naval position and the scientific reputation of this great Empire. Notwithstanding troubles, personal sacrifices and regrets necessarily connected with the work, it has been a pleasure and an honour to have taken part in the explorations and researches which mark the greatest advance of the knowledge of our planet since the celebrated geographical discoveries of the 15th and 16th centuries."

He was never tired of exploring the sea, and in 1880 and 1882 he took part in two expeditions to explore the Faroë Channel in H.M.S. "Knight Errant" and H.M.S. "Triton." He established marine laboratories first of all at Granton on the Firth of Forth, and later on the Clyde at Millport, Cumbrae. Between 1883 and 1894 he was continuously exploring the West coast of Scotland in his small steam yacht "Medusa," which was specially fitted for carrying on oceanographical investigations, and in these he was assisted by Mr. J. T. Cunningham, Dr. H. R. Mill, and many naturalists.

He never spared himself, and when he was approaching his 70th birthday he embarked on the "Michael Sars," a steamer no bigger than an ordinary fishing trawler, with a gross tonnage of 226 and with but 300 h.p. engines, to cross the Atlantic on a scientific expedition, the profoundly important results of which he published in collaboration with Dr. Johan Hjort in the well-known book, 'The Depths of the Ocean.' He was very capable of getting on terms with the sailor men, and had a thorough knowledge of the sailor's mode of life and the sailor's point of view, and, it may perhaps be mentioned, of the sailor's vocabulary. Although he became 73 a few days before the tragedy, he seemed, and was, in fact, a much younger man, "good for at least another 10 years," as a leading physician, who knew him well, remarked to me some weeks ago.

He took a great interest in the project for establishing a meteorological observatory on the top of Ben Nevis. He was Secretary of the Committee which raised the necessary funds, and largely through his efforts £5000 was soon collected. He was one of the Directors of the Observatory until, unfortunately, it was closed a few years ago. For several years he was a scientific member of the Scottish Fishery Board, and he represented the British Government at the International Fisheries and Hydrographic Conference in Stockholm in 1899, and he was President of the Geographical Section of the British Association in 1899. The same year he delivered the Lowell Lectures at Boston, U.S.A., and again in 1911 he delivered a second course of lectures at the Lowell Institute. For many years he ungrudgingly gave his services as one of the Secretaries and Member of the Council and Vice-President of the Royal Society of Edinburgh, and the societies with which he was actively connected are almost as numerous as the honours which in later days were showered upon him. At the time of his death he was President-elect of the Meteorological Conference to be held in 1914 at Edinburgh, and was actually engaged in making arrangements for a successful meeting the day before his tragic end.

Sir John held strong views on Education. He had little use for the "grand fortifying curriculum" of the Classics, but I shall never forget how indignant he was with me when a few years ago I was unable to produce at almost a moment's notice a tutor for his son, who was to be at once "a first-class classic and a thoroughly trained oceanographer." His son was then reading for the Previous Examination and embarking on a voyage round the world.

Apart from his science, which would have occupied the entire time of most men, Sir John was latterly also interested in commerce. A bit of material included among a collection of deep-sea deposits from the neighbourhood of Christmas Island in the Indian Ocean enabled him to recognise that that remote island contained valuable phosphatic deposits. The island was quite uninhabited, but obviously a source of wealth, and he urged the Government to annex the island. Ultimately they did so, and Sir John obtained a lease of it along with Mr. Ross, of the Cocos Islands. A company was formed to develop its resources, and Mr. C. W. Andrews, of

the Geological Department of the British Museum, was granted leave of absence for a year, and in 1897-8 he visited and explored the island, Sir John paying all the expenses and presenting the specimens Mr. Andrews collected to the British Museum. The Trustees in 1900 published the result of the researches in a monograph, which is a most interesting record of the indigenous animals and plants of a lonely oceanic island both before the arrival of civilised man and after.

Sir John himself on several occasions visited Christmas Island, and crossed it from end to end. Valuable deposits of phosphates were found, water was discovered, clearings were made, a railway laid down, waterworks and piers constructed, aerial haulage erected, and houses built. The island now maintains a population of about 1500, composed of Europeans, Colonials, Chinese, Malays, Sikhs, etc., and a flourishing business is being carried on in the export of phosphates. Plantations of rubber, hemp, coconuts, bananas, papaws, cotton, etc., have been established with more or less Sir John always looked upon this development as an indirect result of the scientific work of the "Challenger" Expedition, and an excellent argument for such research work being carried on by the Government. He knew that His Majesty's Treasury had received in hard cash within the past 15 years, in the form of rents, royalties, and taxes, a sum greater than the cost to the country of the whole "Challenger" Expedition, and he recalled how, during the time the money was being annually voted for the issue of the "Challenger" publications, many Members of Parliament objected to public money being voted for such a purpose.

To enumerate the various honorary degrees, honorary memberships of learned Societies, medals and decorations of all sorts that Sir John received would occupy too much space. The more important of them are set out in 'Who's Who,' but he always held that they were conferred on the Expedition rather than upon himself.

In stature Sir John was short, broad shouldered, with a finely poised, distinguished head. His complexion was fair and his blue eyes piercing. His was a personality that could not be overlooked in any company. He was at times brusque, rather domineering, very confident of his own opinion, and he liked to have his own way, and, indeed, he generally got it, but he was most kind and most helpful to his assistants, and he spent his wealth largely in promoting the advance of science. He was singularly straightforward, and at times almost blunt, but he did not understand or appreciate the methods of the politician. If he was once your friend he remained your friend. Rather late in life he married in 1889 Isabel, only daughter of the late Mr. Thomas Henderson, of the well-known Anchor Line of Glasgow. He was a devoted husband and father, and although he had unconventional ideas about the education of his children he was profoundly attached to them, and was never happy unless he had one or other with him.

Sir John Murray was instantaneously killed in a motor accident near Edinburgh on March 16, 1914.

A. E. S.

WILLIAM GRYLLS ADAMS, 1836-1915.

WILLIAM GRYLLS ADAMS was born on February 16, 1836, at Lidcot, Laneast, Cornwall, being the youngest son of Thomas Adams, who had married Tabitha Knill Grylls, of Budharlick, the owner of a small estate. Both families had been farmers in the neighbourhood as far back as records can be traced. The marriage resulted in a family of four sons and three daughters, the eldest son, born in 1819, being the renowned John Couch Adams, the discoverer of the planet Neptune.

William Grylls Adams was educated at a private school at Birkenhead, and afterwards at St. John's College, Cambridge, which he entered in 1855. He graduated as Twelfth Wrangler in 1859; and was elected to a Fellowship at St. John's in 1865. After leaving Cambridge he acted for about a year as Vice-Principal of the Peterborough Training College, and then, for three years, as a mathematical master at Marlborough. In 1863 he was appointed Lecturer in Natural Philosophy at King's College, London, where the Professorship was then held by Clerk Maxwell. After Maxwell's retirement, Adams was, at Easter, 1865, appointed to succeed him, and he retained the Chair for forty years, till the summer of 1905. Adams early recognised the importance for students of Natural Philosophy that they should have the opportunity of taking part in practical experimental work, and, as the result of his efforts, a Physical Laboratory was opened for the instruction of students at King's College in October, 1868.

As a professor, Adams made teaching his main occupation, but he by no means neglected original work. In 1877 he published in the 'Philosophical Transactions,' in conjunction with his pupil, Mr. R. E. Day, an important experimental investigation of the electrical effects produced by the action of light on selenium. And previously, in 1875, a paper on the experimental determination of the lines of flow and equipotential surfaces in conductors of two and three dimensions was chosen as the Bakerian Lecture before the Royal Society. In this paper Adams followed up and considerably extended the previous work in the same direction of Kirchhoff and Quincke.

He took an active part in the foundation of the Physical Society of London, of which he was President for the years 1878-80. One of his communications to it was an account of a new measuring polariscope. He was President of the Mathematical and Physical Section of the British Association at the Swansea meeting in 1880, and was President of the Society of Telegraph Engineers and Electricians (now the Institution of Electrical Engineers) for the year 1884. In his Presidential Address he gave some valuable results of the experimental measurement of the efficiency of dynamos, carried out chiefly in connection with the Electrical Exhibition held at the Crystal Palace in 1882. He also communicated to

the Society a paper on the use of alternate current dynamos as motors, chiefly founded on experiments carried out at the South Foreland Lighthouse. In 1885 he carried out for the Trinity House, at the South Foreland, experiments on the comparative value for lighthouse purposes of oil and the electric light. He was for many years a member of the Kew Observatory Committee of the Royal Society (since amalgamated with the administration of the National Physical Laboratory), and was also a member of the Board of Visitors of the Royal Observatory, Greenwich. It was probably his connection with these bodies that led to his giving special attention to Terrestrial Magnetism. He wrote several papers on the simultaneous disturbances of the magnetic elements at different parts of the earth's surface.

In 1896 he issued a volume in which were collected all the scientific papers published by his brother John, who had died in 1892. This was followed in 1901 by a second volume, edited in conjunction with Mr. R. A. Sampson, containing the papers, so far as they could be made available, which his brother had left in manuscript.

He was elected a Fellow of the Royal Society in 1872, and served on the Council from 1882 to 1884 and from 1896 to 1898.

As a young man Adams was an enthusiastic mountaineer, and became a member of the Alpine Club as early as 1864. Personally, he was a man of the greatest geniality, and full of good-natured fun. Many must have pleasant memories of the kindly hospitality and hearty welcome which he and Mrs. Adams offered to their many friends at their house in Campden Hill Square.

After resigning his Professorship he went in 1906 to live at Broadstone, Dorset, but continued for some time to come to town occasionally for Royal Society and other meetings. For the last few years, however, his failing memory obliged him to give up more and more completely all public engagements. He died at his house at Broadstone on April 10 of the present year (1915).

In 1869 he married Mary Dingle, of Lewannick, who, with a daughter and two sons, survives him.

G. O. F.

E. H. AMAGAT, 1841-1915.

EMILE HILAIRE AMAGAT was born at Berri (Saint Satur) in 1841. After a sound preliminary education he studied physics for several years at the Sorbonne in preparation for the examinations for the higher teaching posts. After acting for some time as assistant at the Collège de France, he held the Professorship of Physics at Fribourg in Switzerland for a few years; he was then elected to the Chair of Physics at the Catholic University of Lyons, where he remained until 1892. He then returned to Paris, where at first he had no definite post, but he was afterwards made a teacher and, later, an examiner at the École Polytechnique; he carried out the duties of the latter post until his death.

Amagat was a simple, modest, and unassuming man, but he possessed extraordinary vigour and enthusiasm for work, and his fearlessness in attacking the most serious experimental difficulties was rewarded by magnificent results. He was not only a brilliant experimenter, but a most ingenious and expert constructor, nearly all the apparatus he employed having been made either by himself or by a skilled mechanic whom he had trained. Amagat himself very truly states that under no other conditions would it have been possible for him to carry out his researches successfully.

Amagat's great conscientiousness is well shown by an incident, the particulars of which have been furnished very kindly by Dr. Guillaume. In the viva voce examination for entrance into the École Polytechnique, about two-thirds of the candidates are usually rejected, and a change of examiners during the process of selection would be liable to produce unfair results. While holding this examination Amagat had a slight apopleptic stroke, resulting in partial paralysis, but he insisted on continuing the work, and had a bed placed near the examination hall, so that, when overcome by fatigue, he could retire and rest from time to time.

During his period of study at the Sorbonne Amagat made a careful study of Regnault's celebrated memoirs, the importance of which greatly impressed him, and between 1867 and 1871, as a preparation for his thesis for the doctorate, he carried out his first considerable research on the influence of temperature on the deviations from Boyle's law, and on the coefficient of expansion of gases under normal pressure. In the course of the next six years Amagat studied the compressibility of liquids at temperatures between 0° and 100° C. and at pressures from 1 to 40 atmospheres.

He realised, however, the importance of greatly extending the range of pressure in investigating the properties of gases, and between 1876 and 1890 he carried out the wonderful series of researches with which his name will always be associated.

The range of pressure was extended in both directions. Between 1876 and 1882, making use of a differential manometer, Amagat determined the

compressibility of hydrogen and carbon dioxide from the atmospheric pressure to 2 or 3 mm. of mercury, while with air he made measurements down to 0.3 mm. At these lowest pressures Amagat concluded that the gases followed Boyle's law within the limits of experimental error. Determinations of the compressibility of rarefied gases are very liable to errors, the data obtained by a number of other investigators being highly contradictory, but the accuracy of Amagat's results has been amply confirmed by those of Lord Rayleigh, who made a most remarkable extension of the range of low pressures.

As regards high pressures, Amagat determined the compressibility of nitrogen up to 430 atmospheres at temperatures from 0° to 100°, with open steel manometer tubes containing mercury. In order to support these tubes, he first made use of a tower of the church of Fourvière at Lyons, and was thus able to take measurements up to 80 atmospheres. A much greater range, with greater constancy of temperature, was afterwards attained by attaching the tubes to the side of a mine shaft in the Saint-Étienne Colliery at Verpilleux. The manometer consisted of lengths of steel tubing screwed together, terminating in a glass tube, to allow of the height of the mercury column being read directly.

Having now determined the deviations from Boyle's law in the case of nitrogen, Amagat was able to employ a nitrogen manometer in the laboratory, and to determine the compressibility of oxygen, air, hydrogen, methane, ethylene, carbon monoxide, and carbon dioxide up to a pressure of 430 atmospheres.

But Amagat was not satisfied with this great step in advance, and in order to measure still higher pressures he constructed in 1886 a manometer on the principle of that of Gally-Cazalat. It may be described as a reversed hydraulic press, the pressure being measured by a column of mercury, the height of which bears the same ratio to that of an open column corresponding to the actual pressure as the cross-section of the small piston does to that of the large one. The original Gally-Cazalat instrument was very defective, but by the introduction of important modifications it was found possible to prevent all leakage and to obtain sufficiently accurate measurements of pressures exceeding 3000 atmospheres.

The glass volume tubes were enclosed in strong blocks of metal and were subjected to pressure both externally and internally, so as to avoid rupture; readings of volume were taken by the method of electrical contacts recommended by Tait. This method was found unsuitable for temperatures higher than 50°, and could not be employed when many readings close together had to be taken, as, for example, in the neighbourhood of the critical point. A very ingenious method was, however, devised by which direct readings could be taken, and was employed for pressures up to 1000 atmospheres and for temperatures as high as 260° C.

The gases examined by means of these two forms of apparatus were oxygen, hydrogen, nitrogen, air, carbon dioxide, and ethylene, and the com-

pressibility of the following liquids was also determined: Water; ethyl, methyl, propyl, and allyl alcohols; acetone; ethyl chloride, bromide, and iodide; carbon disulphide and phosphorus trichloride.

The researches relating to the compressibility of fluids necessarily involve determinations of the deformation of the containing vessels and of the absolute compressibility of mercury. Amagat first verified the formulæ relating to elasticity in the case of circular cylinders with plane bases, and determined the coefficient of Poisson and the coefficient of elasticity for glass, flint glass, steel, copper, brass, Δ metal, and lead, and he then carried out determinations of the compressibility of glass and flint glass up to 2000 atmospheres at 0°, 100°, and 200°, by a method somewhat resembling that employed for the measurement of cubical dilatation by means of linear dilatation.

In order to determine the absolute compressibility of mercury Amagat employed long tubes of glass and of flint glass filled with mercury, which he compressed both internally and externally in order to ascertain the apparent compressibility. The absolute compressibility was then calculated by difference.

The abnormal behaviour of water in many respects led Amagat to make a special investigation of this substance, and he found that the point of maximum density was lowered by raising the pressure, reaching 0° under a pressure of less than 200 atmospheres.

Amagat also made important investigations of the effect of pressure on the freezing points of liquids; in the case of tetrachlorethylene the freezing point was raised from -19.5° to $+19.5^{\circ}$ by increasing the pressure from 210 to 1160 atmospheres.

In tabulating his results Amagat does not give the volumes occupied by a gramme, but by such a mass of each substance as would occupy unit volume in the gaseous state at normal temperature and pressure. The general results are clearly shown by graphs in which the co-ordinates are PV and P.

Among the more interesting points brought out by Amagat may be mentioned the following:—

- 1. For hydrogen the isotherms, at all the temperatures studied, are straight parallel lines; hence p(v-a) = b, where a and b are constants.
- 2. For all the other substances the value of PV falls with increase of pressure to a minimum and then rises again, the fall becoming more and more abrupt as the temperature is lowered. The form of the isotherm, starting from the minimum, is slightly curved.
- 3. Straight lines of equal volume (PV/P = V) are intersected at equal distances by the isothermals, drawn at intervals of 10° , in the case of both carbon dioxide and ethylene. In other words, taking temperatures as abscissæ and pressures as ordinates, the isochors are straight lines, or P = cT a. This relation was discovered independently by Barus and by Ramsay and Young; it is probably very nearly but not absolutely true.

4. The locus of the minimum values of PV is a parabola with respect to the horizontal axis. The coefficients $\Delta V/\Delta t$, $\Delta P/\Delta t$, $1/V \cdot \Delta V/\Delta t$, and $1/P \cdot \Delta P/\Delta t$, were examined in great detail.

When Amagat returned to Paris in 1892 he was unable to obtain the use of a laboratory in which he could continue his experimental investigations, and the last 21 years of his life were spent in compiling and co-ordinating the immense number of numerical data resulting from his previous work. The results were published in a brochure entitled, "Notes sur la Physique et la Thermodynamique." Among the more important subjects dealt with may be mentioned:—(1) The specific heat of gases, (2) the internal pressure of fluids, (3) the corresponding states of matter.

- 1. Combining his own results with those of Prof. Joly on the specific heat of carbon dioxide at constant volume between 0° and 100° under a pressure of about 100 atmospheres, he was able to calculate the ratio of the specific heats for this substance and to show the great variation of the ratio for pressures between 50 and 100 atmospheres at 50°. He also proved the discontinuity of the specific heat during change of state from liquid to saturated vapour.
- 2. Amagat arrived at the conclusion that the two functions (Tdp/dt-p) and $(p_0v_0/v-p)$, starting from sufficiently great molecular distances (greater in the latter case than in the former), are inversely proportional to the square of the volume, and that when this law is followed the interpolecular attraction is inversely proportional to the fourth power of the distance. In the course of this research he was led to an exact and unexpected method of calculating the value of the absolute zero point.
- 3. By a simple and ingenious method of projection Amagat was able to prove the approximate correctness of the law of corresponding states without the necessity of ascertaining the actual critical constants. He arrived at the conclusion that, at any corresponding points whatever, the value of PV/T is (approximately) the same for all substances.

The great value of Amagat's work was recognised both in France and in this country. On the death of Alfred Cornu, Amagat was elected to take his place in the Académie des Sciences, and he was awarded the Prix La Caze by that body. He was at one time president of the Société de Physique, and was afterwards made an honorary member of the Society. He was a Foreign Member of the Royal Societies of both London and Edinburgh.

Amagat's work was inspired by that of Regnault, and he may be regarded as the great successor to that great physicist.

S. Y.

HENRY WILLIAM LLOYD TANNER, 1851-1915.

The father of Henry William Lloyd Tanner was Prof. Henry Tanner, F.C.S., a well-known writer on Agriculture and Agricultural Chemistry, who served on one or more Royal Commissions. The son was born at Burham in Kent, on February 17, 1851. He was never talkative about himself, even at home, so that few facts are known about his young days. His school was Bristol Grammar School, which has turned out many an able mathematician, and has supplied Oxford in particular—Tanner's University—with a considerable number of strong men in learning, education and affairs. He must have left school young; for when in October, 1868, he came up to Jesus College, Oxford, as Natural Science Scholar he had already spent a year at the Royal School of Mines (where he had formed a friendship that was used against him later) and had secured his diploma there.

At Oxford he soon showed his bent for Pure Mathematics, and research His mathematical tutor was Mr. John Griffiths, an original writer on Elliptic Functions, who happily still lives, and one can imagine how such a tutor welcomed and stimulated such a pupil. Tanner obtained a first class in Mathematical Moderations in 1870, one in the Final School of Mathematics in 1872, and one in Natural Science in 1873. It is a little surprising that he let others carry off the higher prizes open to mathematical students, Fellowships, and the Junior and Senior Mathematical Scholarships; but the days were those of examination for everything, and his is not the only case one can remember of a man with a passion and a genius for investigation who did not allow to himself that the circumstances of the moment called for patient application to uncongenial as well as congenial tasks, and for the cultivation of examination facility. Moreover, he had strong interests outside Mathematics, being a keen musician, a reader of fine literary taste, a Union debater. He was Librarian of the Union in Easter term, 1873, succeeding Mr. E. W. B. Nicholson, afterwards Bodley's Librarian, just between the times at which the present Prime Minister was Treasurer and President.

After leaving Oxford he is believed to have been a schoolmaster for a little while, but was soon appointed Professor of Mathematics and Physical Sciences at the Royal Agricultural College, Cirencester. While there, his fine work on Differential Equations proceeded vigorously, and it looked as if he might long enjoy in the College congenial and not too burdensome duties, with sufficient leisure for research. But there seem to have been elements of unhappiness in the Institution. A "strike" of members of the staff connected with a case of alleged wrongful dismissal terminated in a victory for the employers, and Tanner's resignation was accepted. Finding himself without secure means of livelihood even for one, he marked the occasion by taking a very small cottage for two, and a wife, Miss Helen Alice Edith

Saunders. Common sense may condemn the haste of this, but the results were very happy. He could protect others, but needed even more than most men a protector himself. Mrs. Lloyd Tanner was musical like her husband, like him highly educated and widely read, yet altogether womanly, and she proved a most devoted wife. Often joining her husband in attention to his responsibilities, she contributed in no small measure to his later success. Her death, in 1902, after a long and painful illness, left him an exhausted and failing man.

After the fiasco at Cirencester he held for comparatively short periods masterships at Sherborne and at his own old school, Bristol. But in 1883 the University College of South Wales and Monmouthshire was founded at Cardiff—years had yet to elapse before it became a constituent college of a new, and now flourishing, University of Wales—and he was appointed to the Chair of Mathematics and Astronomy in it, thus entering on a settled life of vast usefulness. While strength lasted, he retained the Chair. During the last illness of Prof. J. Viriamu Jones, and the interregnum which followed its lamented termination in 1901, he directed the College as Acting Principal with marked efficiency. Finally, when all too soon, in 1909, he could work no longer, the Council made him Emeritus Professor on retirement.

As he was taking possession at Cardiff painful incidents occurred. The word went round among certain good Welshmen that he was a secularist, or friend of secularists, whose influence on students might be anti-religious; and some effort was made to upset his appointment. Tanner bore his sensitiveness in private. The man who at Cirencester, in wild indignation because of a real or fancied wrong to another, had been insubordinate, and had suffered for it, now at Cardiff, threatened with a grievous wrong himself, said nothing, but possessed his soul in patience waiting for the storm to pass. And it did pass. Very soon all knew that their professor was no firebrand, but the most lovable and sympathetic of men.

Testimony to the energy and foresight with which he set about the task of organising courses of study, and to the inspiring character of his own teaching, is abundant. Equally abundant, and no less strong, is the testimony to his unfailing courtesy and good humour, to his happy faculty of securing affection from colleagues and generations of students. In the early days of the College—before University dignity was secured—there can have been little scope for the exercise of his gifts in fostering higher study. The requirements must have been for the systematisation of unambitious teaching and for methods suitable to new armies of raw recruits. No exercise of patience was too great for him. I could quote letters from those who worked with him full of warm admiration for his successful devotion, in class and out of it, to the interests of the college, of student life, and of the individual—letters all free from a single word of disparagement. I could give at length the resolution recently communicated by the Council of the College to his family, in which it is shown how strong a sense prevailed in higher College

circles that he had been one of the most highly valued members of the Staff, that he had taken a very deep interest in the welfare of his students and in the general social life of the College, and that he was regarded with warm admiration by colleagues and students alike. But the one appreciation which I choose to give verbatim is that of a peccant undergraduate, taken from a comparative estimate clearly not intended, and not altogether suitable, for publication:—

"But call on old Tanner about a cut lecture, and his smile fairly shouts, 'Well, if it isn't my old pal Jack Owen,' and he treats you as if you'd just got a First, and never rags you about the lecture. But somehow when he's finished you have registered a vow that whatever else you may cut in future it shan't be Maths. And it isn't."

The "old Tanner" in the above is the "old" of endearment; and undoubtedly dons in general are looked upon as really old by undergraduates perhaps ten years younger than themselves. All the same, Tanner never looked young. The light in the eye shone from an apparently care-worn face quite early; and as care grew and strength failed that light began to need kindling by the sight of a friend to be encouraged.

He was elected a Fellow of the Royal Society in 1899; and was also an Associate of the Royal College of Music, a Fellow of the Royal Astronomical Society, and a member of the London Mathematical Society. This last-named society published most of the more important among his mathematical writings. He was an early recipient of the degree of Doctor in Science at Oxford when degrees in recognition of eminence in research were instituted.

He was an excellent man of business—of public and altruistic business at any rate. His mark has been left in the organisation of the mathematical curricula of the Welsh University. He did not go out of his way to seek administrative work, but when it came his way he undertook it and did not spare himself in carrying it out. His valued services as Acting Principal of the College for a time have already been referred to. In 1891 he earned golden opinions by his discharge of the operous duties of a Local Secretary on the occasion of the meeting of the British Association at Cardiff. His services to education—as to the value of which he was an enthusiast—were not confined to the College and University. For several years he was on the Glamorganshire Governing Body for Intermediate Schools, working thereon with keen interest, and being greatly missed when he retired from it. He was a Governor of the Penarth County Schools. In another field mention must be made of his efforts for the encouragement of Music in Cardiff. many years he was a vice-president and active supporter of the Cardiff Musical Society.

Soon after his wife's death in 1902 it became clear that he had overtaxed his powers. Failure in bodily strength began to be accompanied by lapses of memory and dazed intervals in the midst of effort. His amazing power of accountration was gone, but not his devotion to duty. He struggled on, being with difficulty kept from the lecture room even when acutely ill; but in 1909

it became clear that his retirement from active work could no longer be postponed. There were difficulties, financial as well as other, both for his family and for the College: the days of the Federated Superannuation scheme for Universities and University Colleges were not yet. Self-denial had to be exercised all round; and a small Civil List pension was secured for him. Thus it was made possible for him to end his days in simple comfort. His life in retirement was quiet and uneventful, with nothing painful about it but progressive decay. On March 6, 1915, he passed away peacefully at Exeter.

He leaves two sons and a daughter. The elder son, Evelyn Lloyd Tanner, 8th Wrangler 1903, First Class Natural Science Tripos 1904, has held important posts in the Indian Civil Service, and is, for the moment, a trooper in the Behar Light Horse, straining in vain for permission to go on active service. (Tanner himself had been a keen volunteer in his young days, and was a fine "shot.") The second, Percy Lloyd Tanner, who has adopted a business career, has my best thanks for much help given me in compiling these notes. The daughter, Cicely Marguerite Lloyd Tanner, has inherited her parents' love for music, and may make it her profession, though now she has devoted herself to "Red Cross" work.

Prof. Lloyd Tanner's contributions to mathematical science, omitting some that are comparatively trifling, form two distinct series. There is an early series on Differential Equations, more particularly on Partial Equations of the second and third orders with intermediate integrals, and a later series on the Theory of Numbers, more particularly on Problems of Cyclotomy. Both series show vigorous penetration, and both artistic refinement. The "push and go" are, however, more marked in the former series, and the beauty and taste in the latter.

The papers on Differential Equations belong to the years 1875-80, and are to be found in vols. 7-11 of the 'Proceedings of the London Mathematical Society, vol. 16 of the 'Quarterly Journal,' and vols. 5-7 of the 'Messenger of Mathematics.' Some (probably the least important) deal with Pfaff's Theorem and Pfaffian Expressions, but most of them with questions of Solution of Equations of the second and higher orders in two, and more than two, independent variables. For a number of the more conspicuous results obtained, reference may be made to the sixth volume of Forsyth's 'Theory of Differential Equations.' One paper, "On the Transformation of a Linear Differential Expression," stands in somewhat close relation to earlier work of Grassmann's, which was no doubt unknown to the writer; but in general it may be said that Tanner in this series of researches did pioneer work in a department of investigation which was neglected, not only in England, but mostly elsewhere at the time. He makes some reference to very instructive work by Imschenetsky on the theory of partial equations of the first and second orders; but he went far beyond that work, opening up some new ways for equations of the second order, and proceeding to those of the third order. For equations of the second order he obtained many results which, expressed in different form, were much later included in a more complete

investigation by Gosserat, for which see the fourth volume of Darboux's Theory of Surfaces.' There is no reason to think that Gosserat's work was not completely independent of Tanner's; but men less self-effacing than the latter—and perhaps the latter himself, had his full vigour remained to him—would hardly have refrained from pointing out a claim to priority. As regards equations of the third order, which admit of integrals of lower order expressible in finite form, Tanner's investigations were most valuable; and some are standard even now.

It is very remarkable that a man, who was producing work of such quality in steady stream should stop suddenly. The advent of exciting times in his life, followed by immersion in absorbing duty, may have had something to do with this. But, as affording another explanation, I remember the importance which he attached to keeping in touch with the current thought of the day. He had been applying, very brilliantly, the formal methods of the older analysis; and meanwhile others were doing work with modern weapons. Before going further he must allow himself time for a profound study of modernism. Once in congratulating me, with the most graceful kindliness, on a piece of formal work of my own, he was too naïve to keep me from being aware that what he really meant was: "Twenty years ago this would have been charming; but is it not rather late for the sort of thing now?" I am pretty sure that he had once reasoned in this way with himself.

However, he never returned with new tools to the work of his old love. During his first busy years at Cardiff his writings were infrequent and minor. About 1886 began the later period of his productive activity; and the subjects attended to now were the purest of the pure in Mathematics, those studies about number whose difficulties and beauty enchain and fascinate an artistic intelligence when once they have allured it, but which leave unaffected except by wonder the man who pursues Mathematics as knowledge for practical use. His chief papers of the new series are spread over vols. 18-27 of the 'Proceedings of the London Mathematical Society.' All have more or less bearing on what is known as Cyclotomy. roots of unity are arranged in sets or "periods"—mono-basic periods if n is prime. Tanner submits the properties of periods, mono-basic and other, to searching examination. It is probably impossible in few words—and I certainly have not the necessary grasp on the theory—to state clearly the nature and extent of this examination. It is evident, however, that the group-notion was used with great cleverness, and that notable advance was made in methods for the formation of equations satisfied by sums of periods. Prodigious labour must have been required in the detailed analysis, as, for instance, reference to the paper ('Proc. Lond. Math. Soc.,' vol. 24) on "Complex Primes formed with Fifth Roots of Unity" will certify. p. 224 we read: "To give some idea of the facility of the method from the calculator's point of view it may be stated that the determination of the prime factors of two primes selected at random in the second million (viz. 1,562,051 and 1,671,781) was completed in three hours." After this, pp. 256-262, comes a full table of results for about 310 primes, results previously obtained by Reuschle being of some service in respect of the first 40.

He never finished all he had to say on these subjects. Very shortly before his powers of concentration began to fail he spoke to me of surprisingly elegant and comprehensive conclusions at which he was arriving, putting aside the natural notion that the mono-basic must first be ransacked, and the poly-basic thus led up to. These conclusions were to remain unrevealed to others.

E. B. E.

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